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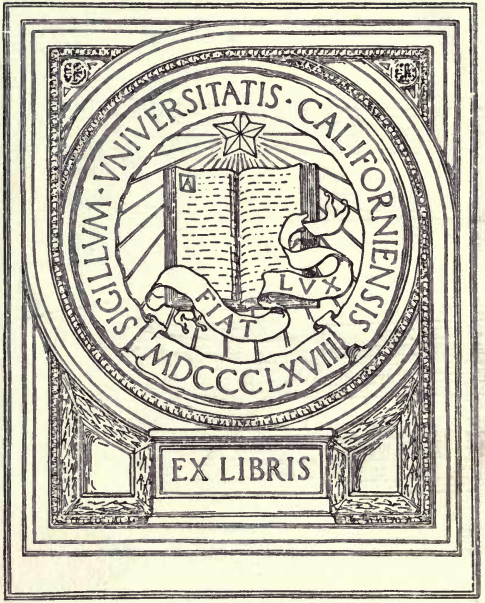
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# PREFACE

THIS book, which forms Part II of a series of textbooks on Organic Chemistry, is intended primarily for the use of students in technical colleges, but it is hoped that it will also prove of value to those who are pursuing a University course of study.

In writing the book particular care has been taken to obtain information as far as possible from the original sources, thus eliminating several errors that appear to have been passed on from textbook to textbook for many years. For details of technical practice Lunge's well-known treatise has been consulted.

A new and highly desirable feature of the book is the section on practical manipulation and qualitative analysis. Though this necessarily deals with the subject much less fully than another book of this series, yet it is hoped that by this means the practical and theoretical sides of the work will be brought into much more intimate connexion.

The author desires to express his indebtedness to Dr. J. B. Cohen, F.R.S., for many valuable suggestions and criticisms.

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# AN ORGANIC CHEMISTRY FOR TECHNICAL INSTITUTES

## CHAPTER I

### THE AROMATIC SERIES

BEFORE the commencement of the modern era of chemistry, when, led by the great chemists of the earlier part of the nineteenth century, among whom the names of **Liebig, Wöhler, Laurent, Gerhardt, Bunsen** and **Hofmann** are prominent, investigators began to recognise the importance of classifying compounds according to their constitution, it had been the custom to arrange in groups substances which possessed similar physical properties. Thus all gases were classified as "airs," volatile compounds as widely dissimilar in constitution as hydrogen chloride, nitric acid, ethyl alcohol, ethyl nitrite and pinene were all "spirits" and "butter of antimony" (impure antimony trichloride) and butter (a mixture of glyceryl esters) were considered to be analogous substances.

Following the same line of argument the early chemists had classified together many naturally occurring substances such as certain balsams, the oils of almonds, of cloves, of lemon and of wintergreen as "**aromatic substances**," since they all possessed a pleasant aromatic odour.

When these substances were studied more carefully and with a certain preliminary knowledge of aliphatic compounds, it was found that these substances could be more systematically classified as

hydrocarbons, alcohols, aldehydes, acids, etc., and that they were all derivatives of a **parent hydrocarbon benzene**, which possessed the molecular formula $C_6H_6$. It was soon recognised that this substance was quite different in properties and therefore presumably in constitution from any of the types of hydrocarbons then known. Moreover, for many years no one succeeded in converting an aliphatic substance into an aromatic or benzene compound, or *vice versa*, and therefore until comparatively recently the compounds of the aromatic series were studied quite separately from those of the aliphatic series. Within the last thirty years a few examples of the interconvertibility of aromatic and aliphatic compounds have been discovered, but for the following reasons among others it is still convenient to deal with aromatic compounds as a class apart from aliphatic compounds.

### Reasons for the Separate Classification of Aromatic and Aliphatic Compounds

(1) The benzene derivatives form such a large, important and characteristic class that they are more easily studied separately from the aliphatic series.

(2) Aromatic compounds are entirely different in structure to aliphatic compounds, being **carbocyclic**, *i.e.* the skeleton structure is a closed ring of carbon atoms, whereas in the aliphatic series one deals with **open chain** compounds. This new type of structure necessitates further complexities of isomerism than are met with among open chain compounds.

(3) Aromatic compounds contain a higher percentage of carbon than their aliphatic analogues.

This may be readily illustrated by burning some benzene and some petroleum ether (chiefly hexane, $C_6H_{14}$). The former burns with a smoky flame and the latter with a clear white flame. This test is the first to be applied in identifying an organic substance to determine whether the compound is aromatic or aliphatic. Aromatic substances burn with a smoky flame.

(4) Aromatic compounds undergo reactions which are peculiar to this series and are not met with in the aliphatic series, e.g. *Nitration*, *Sulphonation*, *Diazotisation* and the *Friedel-Crafts*, *Perkin* and *Reimer* reactions.

(5) The hydroxy and halogen derivatives of benzene differ from those of the paraffins in being respectively acidic and usually unattacked by alkalis.

## CHAPTER II

### THE FORMULA FOR BENZENE

BEFORE the aromatic compounds can be studied in detail it is necessary to determine the structural formula of benzene, the parent hydrocarbon of the series. This problem was for the greater part solved in **1865** by **Kekulé**, who based his conclusions on the following experimental evidence:

(1) The empirical formula as determined by a combustion is **CH.**

(2) The vapour density is 39, the molecular weight therefore 78 and the molecular formula $(CH)_6$.

(3) Benzene behaves chemically as an unsaturated compound with three olefinic linkages, not so inert as a paraffin but **not so chemically reactive as an olefine.** Thus it does not decolorise potassium permanganate or bromine water like an olefine, but on heating in a sealed tube with hydriodic acid (the most powerful reducing agent known) it yields **hexahydrobenzene,** $C_6H_{12}$, and on exposure to chlorine and sunlight it slowly forms **hexachlorobenzene,** $C_6H_6Cl_6$.

(4) If we attempt to arrange $C_6H_6$ as a straight chain compound we invariably arrive at an olefinic or acetylenic derivative and the properties of benzene do not conform to those of this type of substance.

A straight chain isomer of benzene is known and has the formula $CH \vdots C . CH_2 . CH_2 . C \vdots CH$. It is known as **dipropargyl** and is prepared by the following series of reactions:

$$2CH_2 : CH . CH_2I \xrightarrow{2Na} CH_2 : CH . CH_2 . CH_2 . CH : CH_2 \xrightarrow{4Br}$$

Allyl iodide — Diallyl

$$CH_2Br . CHBr . CH_2 . CH_2 . CHBr . CH_2Br$$

Diallyl tetrabromide

$$\downarrow \text{Alc. KOH}$$

$$CH \vdots C . CH_2 . CH_2 . C \vdots CH$$

Dipropargyl

This substance behaves as a true acetylene forming an octabromide and explosive silver and copper salts.

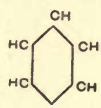
*The only alternative is to arrange the carbon atoms in the form of a ring.*

(5) Benzene derivatives even throughout a long series of reactions **retain their $C_6$ grouping.** Only very violent oxidising agents will rupture this and then the whole molecule breaks down, usually to carbon dioxide.

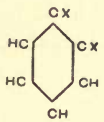
(6) **Only one mono substitution product** can be obtained from benzene; thus there is only one chlorbenzene, though it may be prepared in many different ways.

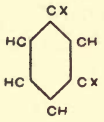
Three and only three isomeric di-substituted benzene derivatives are obtainable.

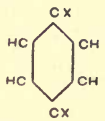
From (4), (5) and (6) it follows that benzene must possess the structure:



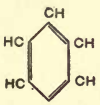

It is obvious that when once the $C_6$ grouping is broken complete disruption of the benzene molecule ensues. As the molecule is **quite symmetrical** only one mono-derivative is possible while the three di-derivatives will possess the formulæ:



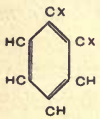

The final difficulty lies in the disposal of the fourth valencies of the carbon atoms. Kekulé at first suggested the formula:




This would account for the unsaturated nature of benzene and the formation of a hexahydride and hexachloride, while at the same time as these unsaturated groups are arranged in a closed ring system one would hardly expect the reactivity of an olefine where the double linking is in an open chain. (See also *Thiele's Theory*, p. 7).

It is obvious, however, that this **static formula** is not satis-

factory since the following two adjacent di-derivatives would be possible:

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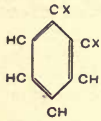
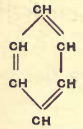
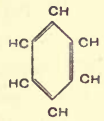



II.

the C atoms attached to X in I. being joined by a double and in II. by a single linkage. Kekulé then modified his formula by suggesting that the **fourth valencies of the carbon atoms were in perpetual oscillation** between the extreme positions:

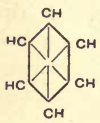



and




This **dynamic formula** effectually disposes of the above objection. Several other formulæ have been suggested, the most important being the **centric formula** proposed by **Armstrong** and **Baeyer.**

Armstrong suggested that the fourth valencies of each carbon atom were directed towards the centre of the ring and were mutually satisfied.

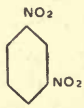



This of course represents statically the mean position of the oscillating bonds in Kekulé's modified dynamic formula.

Until more definite evidence has been obtained it is customary to write simply the bare hexagonal skeleton:

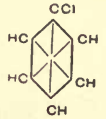
a CH group being supposed to be present at each angular point. Derivatives are written as follows:

Chlorbenzene

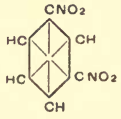



Di-nitrobenzene

instead of in the more cumbersome way




or




The radical $C_6H_5$ is known as the **phenyl** group. The aromatic analogues of the alkyl radicals, typical groups being phenyl, $C_6H_5$, and benzyl, $C_6H_5 . CH_2$, are termed **aryl** radicals.

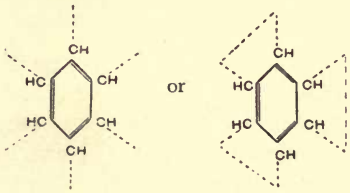
**Thiele's Theory.**—Thiele when studying the action of bromine on compounds of the type $R_2C=CH-CH=CR_2$ found that when one molecule of bromine was employed the resulting compound was not $R_2CBr.CHBr-CH=CR_2$ as one would expect, but $R_2CBr-CH=CH-CR_2Br$. Similarly on gentle reduction the product was $R_2CH-CH=CH-CHR_2$, not $R_2HC-CH_2-CH=CR_2$. He explains these facts by assuming that doubly bound carbon atoms possess a further slight **residual valency** which may be indicated by a dotted line, *e.g.* $R_2C=CH-CH=CR_2$. In a **conjugated system** of double bonds (*i.e.* alternate single and double linkages) the two middle residual valencies neutralise each other thus:

$$R_2C=CH-CH=CR_2.$$

On the introduction of two atoms of bromine these attach themselves to the carbon atoms possessing free residual valency and the compound

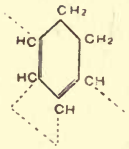
$$R_2C(Br)-CH=CH-CR_2(Br) \text{ results}$$

Benzene if written in accordance with this theory becomes:

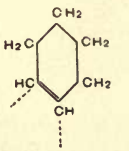



Since the residual valencies neutralise one another the compound is not markedly unsaturated as an olefine would be.

If now we reduce benzene to dihydrobenzene we obtain:




This compound according to the Thiele theory should behave like an olefine as it has unsaturated residual valencies, and on further reduction should give:




These compounds are actually produced and have a typical olefine character, reducing finally to hexahydrobenzene.

### Nomenclature of Isomeric Benzene Derivatives

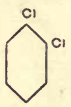
Experiment shows that only one mono-derivative of benzene can be obtained. With di-derivatives, however, three isomers are possible, viz. :

Ortho

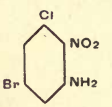
Meta

Para

These are known respectively as *ortho*, *meta* and *para* di-derivatives.

Thus :  is orthodichloro-benzene and parabromonitro-benzene.

With tri- and tetra-derivatives this system is not convenient and the carbon atoms of the ring are therefore numbered :



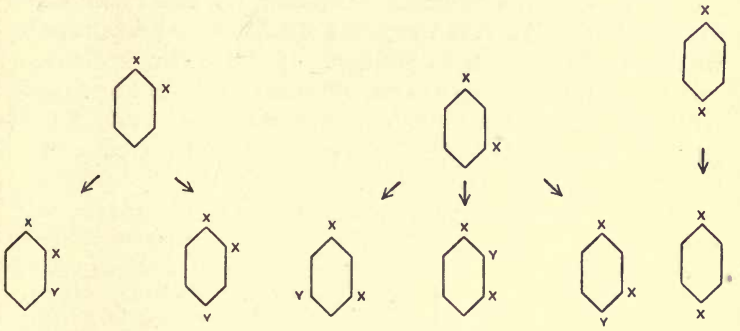
would therefore be called 1 chlor 2 nitro 3 amino 5 brombenzene. As the ring is perfectly symmetrical, however, one may commence numbering from any point, so the above compound could equally well be named 3 chlor 4 nitro 5 amino 1 brombenzene.

**Orientation** (French, *orienté* = situated). — Orientation (*i.e.* determination of the relative positions of substituent groups) of a benzene derivative is obviously a very necessary and important process. It is usually carried out by *conversion of the substance of unknown constitution by some simple reactions into one of known constitution.* Thus if a given alcohol on oxidation give rise to a known meta dicarboxylic acid one would justifiably conclude that the alcoholic groups were in the meta position to one another. This method of course involves a knowledge of the orientation of some simpler compounds.

A method which is based on first principles and requires no previous knowledge of the orientation of any compounds is

known as **Körner's Absolute Principle of Orientation.** This rests on the following reasoning:

If we introduce into an *ortho* disubstituted benzene compound one other substituent group two isomeric compounds are obtained. With a *meta* compound three isomers and with a *para* compound only one product results.



To take a practical example:—Suppose we wish to find whether a given dichlorbenzene is an ortho, meta or para compound. The substance is further chlorinated or nitrated to introduce a third substituent and the product is fractionally crystallised or distilled. If two isomeric substances can be separated from the reaction product the original dichlorbenzene was an ortho compound, if three a meta compound, while if the product consists entirely of one compound the initial material was a para compound.

Though the introduction of a second substituent into a mono-derivative gives rise to a mixture of three isomers (*o*, *m* and *p*), one usually finds that the relative quantities produced vary greatly with different groups; thus if nitrobenzene is chlorinated the product consists almost entirely of *m*-chlornitrobenzene, only traces of the other isomerides being produced. If on the other hand chlorbenzene is nitrated a mixture containing considerable quantities of *ortho* and *para* but very little *meta* nitrochlorbenzene results. A rule for predicting which isomer will be produced to the greatest extent has been formulated by **Crum Brown** and

**Gibson.** The rule is wonderfully reliable, though it is purely empirical.

### Crum Brown and Gibson's Rule of Substitution

In a compound RX where the substituent group already present is X, **if the hydrogen compound HX can be directly oxidised to the hydroxyl compound HOX any new substituent will go chiefly in the meta position.** If HX cannot be directly oxidised to HOX the new group will enter in the ortho or para position. As a general rule both isomerides are produced, the relative proportions depending on the particular groups, the temperature and other conditions.

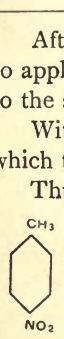
A few examples will illustrate the application of this rule.

| Compound. | X. | HX. | HOX. | Position taken by any New Substituent. |
|---|---|---|---|---|
| $C_6H_5Cl$ | Cl | HCl | HClO | *o* or *p* |
| $C_6H_5Br$ | Br | HBr | HBrO | *o* or *p* |
| $C_6H_5NO_2$ | $NO_2$ | $HNO_2$ | $HNO_3$ | *m* |
| $C_6H_5NH_2$ | $NH_2$ | $NH_3$ | $NH_2OH$ | *o* or *p* |
| $C_6H_5.CHO$ | CHO | HCHO | HCOOH | *m* |
| $C_6H_5.SO_3H$ | $HSO_3$ | $H_2SO_3$ | $H_2SO_4$ | *m* |
| $C_6H_5CH_3$ | $CH_3$ | $CH_4$ | $CH_3OH$ | *o* or *p* |
| $C_6H_5COCH_3$ | $CH_3CO$ | $CH_3CHO$ | $CH_3COOH$ | *m* |
| $C_6H_5COOH$ | COOH | HCOOH | $H_2CO_3$ | *m* |
| $C_6H_5OH$ | OH | $H_2O$ | $H_2O_2$ | *o* or *p* |

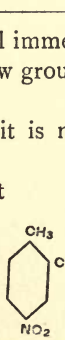
After a little practice one can tell immediately without having to apply the rule what position a new group will take up relative to the substituent already present.

With a disubstituted compound it is not always easy to say which tri-derivative will result.

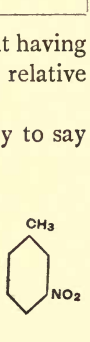
Thus we could say definitely that




on chlorination would give




but with



a difficulty arises. In general no rule is applicable, but it may be remembered that an alkyl group has very little directive influence, so in the latter case the product would consist almost entirely of 1 methyl 3 nitro 5 chlorbenzene. Hydroxyl and amino groups on the other hand exert a powerful influence, ortho and para derivatives being invariably obtained.

### Synthesis of Benzene Derivatives from Open Chain Compounds.

(1) If acetylene is heated in a closed tube for some days at a red heat a certain amount of polymerisation results with the formation of benzene:

$$3\,C_2H_2 \rightleftarrows C_6H_6$$

(2) Methylacetylene (allylene) treated with sulphuric acid or on heating polymerises to **mesitylene** (1 . 3 . 5 trimethylbenzene).

$$3\,CH \equiv C \,.\, CH_3 = C_6H_3(CH_3)_3$$

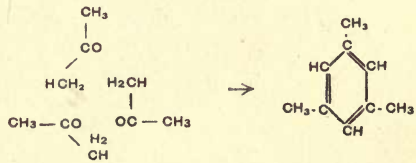
Dimethylacetylene (crotonylene) in the same way yields hexamethylbenzene.

(3) Propiolic acid polymerises in sunlight to benzene 1 . 3 . 5 tricarboxylic acid (trimesic acid):

$$3\,CH \equiv C \,.\, COOH = C_6H_3(COOH)_3$$

(4) Acetone when boiled with concentrated sulphuric acid condenses with the formation of mesitylene:

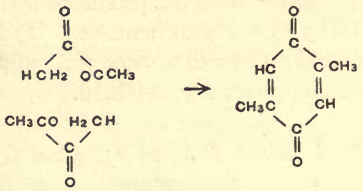
$$3\,CH_3COCH_3 = C_6H_3(CH_3)_3 + 3\,H_2O$$




Methylethyl ketone in the same way yields 1 . 3 . 5 triethylbenzene.

(5) Potasssium at a red heat combines with carbon monoxide to form the explosive compound $C_6(OK)_6$, the hexapotassium salt of hexahydroxybenzene.

(6) Diacetyl on treatment with alkalis yields 2 . 5 dimethyl-quinone (*p*. xyloquinone) :



Diacetyl is made by the following series of reactions :

$$CH_3COCH(CH_3)COOC_2H_5 + HNO_2$$

Methylacetoacetic ester

$$= CH_3CO \cdot C(CH_3) = NOH + CO_2 + C_2H_5OH$$

Diacetyl monoxime

$$\downarrow 15\%H_2SO_4$$

$$CH_3CO \cdot COCH_3 + NH_2OH$$

Diacetyl

(7) Sodiomalonic ester when heated at 140° is converted into phloroglucinol dicarboxylic ester (p. 97).

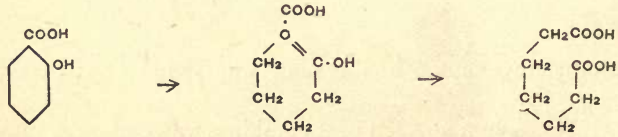
### Decomposition of the Benzene Ring

(1) Benzene when maintained at a red heat breaks down, yielding acetylene :

$$C_6H_6 \rightleftarrows 3\,C_2H_2$$

(2) Picric acid on distillation with bleaching powder yields chloropicrin, $CCl_3 \cdot NO_2$.

(3) Salicylic acid is reduced by sodium and amyl alcohol to a tetrahydro-derivative which, on hydrolysis, yields pimelic acid :



(4) Resorcinol on reduction gives dihydroresorcinol, which may be hydrolysed to γ acetobutyric acid, $CH_3CO \cdot (CH_2)_3COOH$.

## CHAPTER III

## AROMATIC HYDROCARBONS

### Benzene

BENZENE was discovered in 1825 by **Faraday** in the liquid residue from cylinders of oil gas.

It may be prepared in a pure state by distilling benzoic acid with excess of lime:

$$C_6H_5COOH + CaO = C_6H_6 + CaCO_3$$

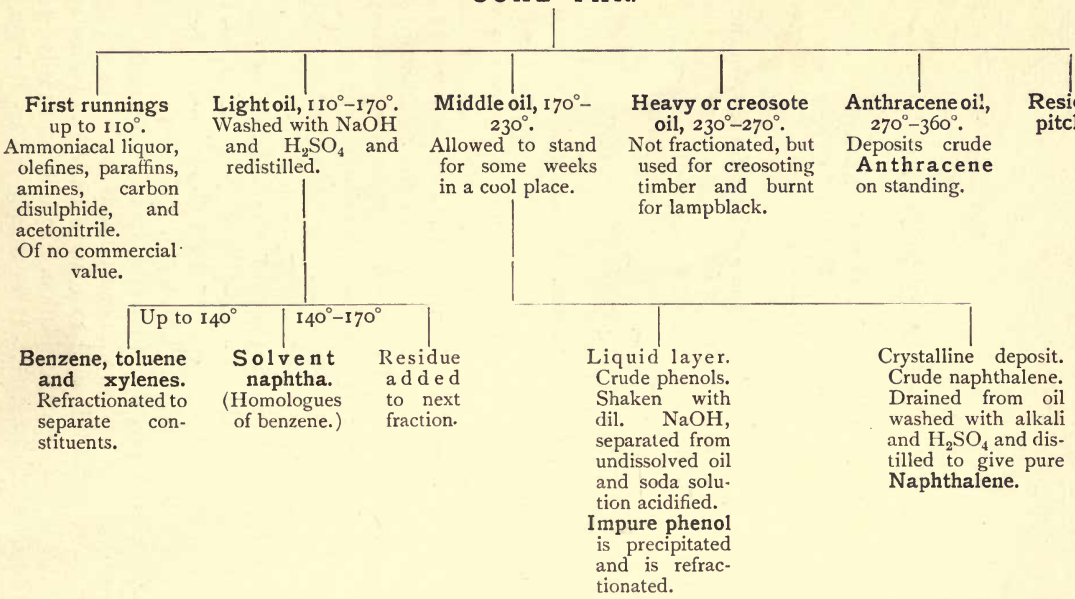
The sole source of commercial benzene and of most of the other aromatic hydrocarbons of technical importance is coal tar. This substance mixed with the *ammoniacal liquor* is produced during the destructive distillation of coal, and after a preliminary separation of the water from the tar the latter is allowed to stand in large tanks where the remainder of the ammoniacal liquor separates from the heavier tar. This process is necessary since tar containing water froths violently on distillation.

The tar is then pumped into iron stills (usually capable of holding 15 tons) and fractionally distilled.

The fractionation is indicated in the table.

The terms "light," "middle" and "heavy" refer to the specific gravities of the distillate, light oil possessing a lower and heavy oil a higher density than water.

**Benzene** is prepared from the first fraction from light oil (which has been washed with caustic soda to extract phenols and with strong sulphuric acid to remove basic substances such as pyridine) by fractional distillation. By this means it is separated from toluene and xylene. It is usually put on the market as


COAL TAR.
First runnings up to 110°. Ammoniacal liquor, olefines, paraffins, amines, carbon disulphide, and acetonitrile. Of no commercial value.
Light oil, 110°–170°. Washed with NaOH and $H_2SO_4$ and redistilled.
Middle oil, 170°–230°. Allowed to stand for some weeks in a cool place.
Heavy or creosote oil, 230°–270°. Not fractionated, but used for creosoting timber and burnt for lampblack.
Anthracene oil, 270°–360°. Deposits crude Anthracene on standing.
Residue pitch.
Up to 140°
140°–170°
Benzene, toluene and xylenes. Refractionated to separate constituents.
Solvent naphtha. (Homologues of benzene.)
Residue added to next fraction.
Liquid layer. Crude phenols. Shaken with dil. NaOH, separated from undissolved oil and soda solution acidified. Impure phenol is precipitated and is refractionated.
Crystalline deposit. Crude naphthalene. Drained from oil washed with alkali and $H_2SO_4$ and distilled to give pure Naphthalene.

**90 per cent. benzol and 50 per cent. benzol,** these numbers indicating not the content of benzene but the percentage of liquid which will distil below 100° C. Further fractionation of 90 per cent. benzol yields nearly pure benzene. A further degree of purification may be obtained by cooling the liquid in ice, when benzene (m.p. 5° C.) freezes out and may be separated from the liquid impurities (*e.g.* toluene, m.p. −90° C.). Benzene retains most persistently a small quantity of **thiophen,** $C_4H_4S$, which is detected by the **indophenin reaction,** a solution of **isatin** in strong sulphuric acid giving a deep blue-green colour with a trace of thiophen. This impurity can only be separated by repeated shaking with cold concentrated sulphuric acid, when it is sulphonated more rapidly than benzene and is thus removed. Thiophen may be obtained from the sulphuric acid extracts by isolating lead thiophen sulphonate and distilling this.

Carbon disulphide, which also usually occurs in ordinary benzene, is detected by the crystalline product formed on standing with phenylhydrazine.

**Benzene** is a colourless liquid freezing at 5° C. and boiling at 80°·5. It is lighter than and insoluble in water, possesses a characteristic odour and is very inflammable, burning with a smoky flame. It is an excellent solvent for oils and for rubber, and is therefore used as a dry-cleaning agent and also for waterproofing, though for the latter purpose **solvent naphtha** (b.p. 140–170) is more generally employed. A considerable part of the benzene made is converted into nitrobenzene and hence into a large range of commercial products, *e.g.* dye-stuffs, perfumes and flavouring essences.

Chemically, benzene is a comparatively non-reactive substance, though not equal to the paraffins in this respect. Ordinary oxidising agents have practically no action on benzene, prolonged action of the most vigorous oxidising a small amount to carbon dioxide and water. If benzene is heated under pressure to 250° C. with hydriodic acid (the most powerful reducing agent known) **hexahydrobenzene,** $C_6H_{12}$, is produced. This compound is more easily produced by the method of **Sabatier and Senderens,** which consists in passing a mixture of the vapour and

hydrogen over reduced nickel powder at 300° C. This method is generally applicable for the preparation of *hydroaromatic* compounds.

Chlorine in sunlight slowly combines with benzene to form an unstable crystalline **hexachloride**, $C_6H_6Cl_6$. This substance readily loses hydrogen chloride, forming 1.3.5 trichlorobenzene. Chlorine and bromine react very slowly with benzene, giving substitution products. The reaction proceeds much more easily in the presence of a "**halogen-carrier**," the most useful of these being the aluminium-mercury couple, iodine, iron powder, ferric chloride, antimony pentachloride and pyridine. In the last five cases the action is evidently due to alternate formation of higher and lower halides. Thus iron powder with bromine yields ferric bromide, which yields up part of its bromine to the benzene, forming bromobenzene and ferrous bromide. The latter combines with more bromine, yielding ferric bromide and the sequence of reactions continues. Similarly iodine is alternately converted into the mono or tribromide. *Iodine compounds cannot be prepared by direct substitution*, as the action $C_6H_6 + I_2 \rightleftarrows C_6H_5I + HI$ goes more readily from right to left. In the presence of iodic acid which removes the hydrogen iodide a certain quantity of iodo compound is however obtainable. Iodo compounds are nearly always made by the **Diazo reaction** (p. 58). Concentrated nitric acid reacts with benzene, yielding a mononitro derivative, $C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O$.

The action takes place more readily in the presence of excess of a dehydrating agent such as sulphuric acid. At a higher temperature *m*-dinitrobenzene is formed.

Benzene slowly dissolves in hot strong sulphuric acid, forming benzene sulphonic acid, $C_6H_6 + H_2SO_4 = C_6H_5SO_3H + H_2O$.

If an acid containing a high percentage of free sulphur trioxide is employed a *m*-disulphonic acid is produced.

**Toluene, $C_6H_5 \cdot CH_3$.**

This hydrocarbon occurs in light oil and is separated from benzene and accompanying hydrocarbons by fractional distillation. It is a liquid of sp. gr. ·87, boiling at 110° C. and freezing at −90° C. It resembles benzene very closely in chemical and

physical properties. On being boiled with oxidising agents such as dilute nitric acid, chromic acid or potassium permanganate the methyl group or "**side chain**" is oxidised to carboxyl, benzoic acid being produced. In the aromatic series side chains of carbon atoms are invariably oxidised to the carboxyl group.

Toluene may be *synthesised* by two important methods.

(*a*) **Fittig's Reaction.**—This is analogous to the **Wurtz** method of preparing paraffins. Equimolecular proportions of chlorobenzene and methyl iodide are dissolved in dry ether in a reflux apparatus and the theoretical amount of sodium in the form of thin slices is added. After the reaction is over the sodium halide is filtered off and the toluene separated from ether and diphenyl by distillation :

$$C_6H_5Cl + CH_3I + 2Na = C_6H_5 . CH_3 + NaCl + NaI$$

(*b*) **Friedel-Crafts' Reaction.**—This reaction is peculiar to the aromatic series. It consists in adding pure anhydrous aluminium chloride to a mixture of an aromatic compound (usually a hydrocarbon) and an aliphatic halogen compound dissolved in carbon disulphide which prevents any undue increase in temperature :

$$C_6H_5.H + Br.CH_3 = C_6H_5 . CH_3 + HBr$$

The aluminium chloride remains unchanged at the end of the reaction.

These are both general methods for the preparation of aromatic hydrocarbons.

The action of chlorine on toluene gives rise to a range of products.

Since toluene consists of an aromatic nucleus and an aliphatic side chain one would expect substitution in the nucleus to give substances resembling the aromatic halogen compounds such as chlorobenzene, while substitution in the side chain should give products resembling methyl chloride in chemical nature. This is found to be the case.

*In the cold with a carrier* chlorine converts toluene into a mixture of *o*- and *p*-chlorotoluenes.

*At the boiling point without a carrier* chlorine substitutes in

the side chain and the progress of the reaction may be followed by finding the increase in weight of the liquid. In this way the reaction may be stopped at any required point and distillation of the product will yield **benzyl chloride**, $C_6H_5 . CH_2Cl$, **benzal chloride**, $C_6H_5CHCl_2$, or **benzotrichloride**, $C_6H_5C . Cl_3$, according to the degree of chlorination. These substances possess none of the properties of aromatic halogen compounds, but resemble the alkyl halides and their derivatives. These compounds are dealt with more fully in the next chapter (p. 24).

**Ethyl benzene**, $C_6H_5 . C_2H_5$, is made, by the Fittig or Friedel and Crafts' reactions, using ethyl bromide or iodide. It is a liquid boiling at 134° resembling benzene and toluene in its properties and reactions. Oxidation converts it into benzoic acid.

**Xylenes**, $C_6H_4(CH_3)_2$. Isomeric with ethyl benzene are ortho, meta and para xylenes, which constitute a considerable proportion of light oil. Since the three isomers have practically identical boiling points (about 140°) they cannot be separated by fractional distillation. As a rule the mixture is not separated, but used as a solvent for rubber and to a certain extent converted into crude xylidine (a mixture of amino xylenes) for the preparation of dye stuffs.

The following methods may be adopted to obtain the pure isomers from the commercial mixture:

(*a*) The mixture is boiled for a considerable time with dilute nitric acid. The ortho and para compounds are oxidised to the corresponding dicarboxylic acids (**phthalic** and **terephthalic** acids), while meta xylene is only slightly attacked and may be separated from the aqueous acid layer. This method, however, entails the loss of two of the isomers.

(*b*) The mixture is shaken with gently warmed sulphuric acid, when the ortho and meta xylenes dissolve forming sulphonic acids. The residual para compound is then separated. The solution of *o*- and *m*-xylene sulphonic acids is then poured into brine, when on cooling the sodium salts of these sulphonic acids crystallise out and may be separated by fractional crystallisation, the ortho compound being less soluble than the meta. The

sulphonic groups are finally split off by heating the salts with dilute hydrochloric acid in sealed tubes:

$$C_6H_3(CH_3)_2 \cdot SO_3H + HO\,H = C_6H_4(CH_3)_2 + H_2SO_4$$

The best way of preparing the pure hydrocarbons is by synthesis.

*o*-**Xylene** is a colourless liquid boiling at 142° and resembling benzene and toluene in its physical and chemical properties. It is best prepared in the pure state by the Fittig reaction using *o*-chlorotoluene, methyl iodide and sodium. Gentle oxidation with boiling dilute nitric acid converts one of the methyl groups into carboxyl when *o*-toluic acid $o\text{-}C_6H_4\begin{cases}CH_3\\COOH\end{cases}$ is obtained.

More vigorous oxidation with potassium permanganate produces the dicarboxylic acid, phthalic acid, $o\text{-}C_6H_4\begin{cases}COOH.\\COOH.\end{cases}$

*m*-**Xylene.** This compound resembles the ortho isomer in its properties and boils at 137°. It is most conveniently prepared in the pure state by gently oxidising mesitylene, $C_6H_3\begin{cases}CH_3\,(1)\\CH_3\,(3)\\CH_3\,(5)\end{cases}$ to **mesitylenic acid,** $C_6H_3\begin{cases}CH_3\,(1)\\CH_3\,(3).\\COOH\,(5)\end{cases}$ This breaks down in the usual way on distillation with lime, yielding meta xylene:

$$C_6H_3(CH_3)_2 \cdot COOH + CaO = C_6H_4(CH_3)_2 + CaCO_3$$

Oxidation yields *m*-toluic acid, $m\text{-}C_6H_4\begin{cases}CH_3\\COOH,\end{cases}$ and finally isophthalic acid, $m\text{-}C_6H_4\begin{cases}COOH.\\COOH.\end{cases}$

*p*-**Xylene** boils at 137° and resembles its isomers in its general properties. It is best prepared by the Fittig reaction, using *p*-chlorotoluene.

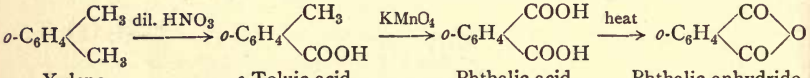
On oxidation it yields *p*-toluic acid, $p\text{-}C_6H_4\begin{cases}CH_3\\COOH\end{cases}$

and terephthalic acid, $p\text{-}C_6H_4\begin{cases}COOH.\\COOH.\end{cases}$

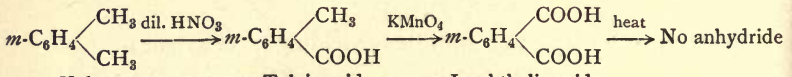
### Orientation of the Xylenes

There are several possible methods of determining the relative positions of the methyl groups in a given xylene. One way, which is theoretically conclusive but practically involves great experimental difficulties, is an application of *Körner's Absolute Method* (p. 9). A nitro group, for example, may be introduced and the product carefully investigated to determine whether one, two or three isomeric nitroxylenes had been produced. A better method would be to oxidise the xylene with dilute nitric acid to the corresponding toluic acid and to identify this by determining its melting-point.

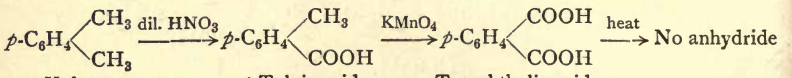
The best method would be to completely oxidise the hydrocarbon to the corresponding phthalic acid and to identify this by the effect produced on heating.




*o*-Xylene — *o*-Toluic acid, m.p. 103° — Phthalic acid, m.p. 213° — Phthalic anhydride, m.p. 128°



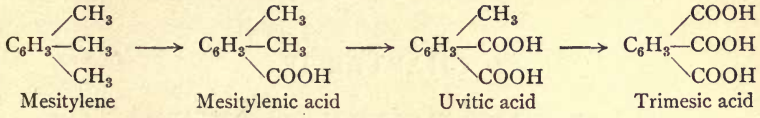

*m*-Xylene — *m*-Toluic acid, m.p. 110° — Isophthalic acid, m.p. 300°




*p*-Xylene — *p*-Toluic acid, m.p. 180° — Terephthalic acid, sublimes

**Mesitylene, 1.3.5 trimethylbenzene** occurs to a certain extent in solvent naphtha, the higher boiling fraction of light oil. It is a colourless liquid boiling at 164° and possessing all the

usual properties of an aromatic hydrocarbon. On oxidation it yields successively mesitylenic, uvitic and trimesic acids, each of the methyl groups being oxidised in turn.




Mesitylene — Mesitylenic acid — Uvitic acid — Trimesic acid

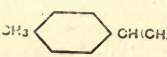
Mesitylene is of interest, as it is readily produced by boiling acetone with strong sulphuric acid (p. 11).

**Pseudocumene, 1.2.4 trimethylbenzene** occurs in solvent naphtha, from which it may be partially separated by careful fractionation. It boils at 169°.

**Cumene, isopropylbenzene** is isomeric with pseudocumene. It is best prepared by the action of zinc methyl on benzal chloride:

$$C_6H_5CHCl_2 + Zn(CH_3)_2 = C_6H_5 . CH(CH_3)_2 + ZnCl_2$$

It may also be prepared by the Fittig and Friedel-Crafts' reactions.

**Cymene**  ***p*-methylisopropylbenzene** is of importance, as it is intimately connected with the terpenes and camphors. It boils at 175°. It may be readily prepared by heating camphor with phosphorus pentoxide, which acts as a dehydrating agent.

$$\underset{\text{Camphor}}{C_{10}H_{16}O} - H_2O = \underset{\textit{p}\text{-Cymene}}{C_{10}H_{14}}$$

Turpentine on oxidation with iodine also yields this hydrocarbon.

$$\underset{\text{Turpentine}}{C_{10}H_{16}} + O = \underset{\textit{p}\text{-Cymene}}{C_{10}H_{14}} + H_2O$$

## CHAPTER IV

## AROMATIC HALOGEN COMPOUNDS

THE following general methods may be employed for the preparation of these compounds:

(1) Treatment of a **hydroxyl compound** with a **phosphorus halide**:

$$\underset{\text{Phenol}}{C_6H_5OH} + PCl_5 = \underset{\text{Chlorobenzene}}{C_6H_5Cl} + POCl_3 + HCl$$

This method is rarely used.

(2) Direct **addition of the halogen** to the substance with or without a carrier. With a carrier nuclear substitution generally results. Without a carrier, particularly in hot solution, substitution occurs in the side chain.

This method is frequently used.

(3) **The diazo reaction** (p. 58). This method is also very frequently used and is the only method available for preparing iodo-compounds.

Aromatic halogen compounds may be divided into **two main classes**:

(*a*) **With halogen in the nucleus.** These compounds are liquids or solids of low melting-point. They possess a characteristic aromatic smell, are insoluble in water and are extremely stable. The halogen can only be removed by the action of sodium (cf. Fittig's reaction). If other groups are also present in the nucleus, as for example in *o*-nitrochlorobenzene, the halogen group is slowly eliminated by boiling with alcoholic potash.

(*b*) **With halogen in the side chain.** These substances, of which benzyl chloride, $C_6H_5CH_2Cl$, is typical, resemble the alkyl halides in reactivity. They are liquids or solids with a

most irritating effect on the skin and eyes. On treatment with sodium hydroxide or moist silver oxide the halogen group is replaced by hydroxyl and an alcohol is produced. With ammonia amines are formed, whilst with silver nitrite nitro-compounds resembling the nitroparaffins result.

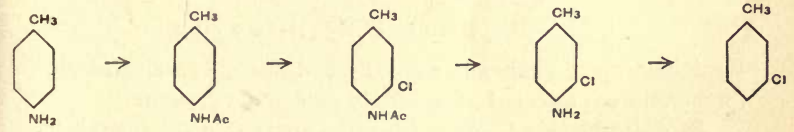
**Chlorobenzene,** $C_6H_5Cl$, is prepared by passing chlorine into benzene containing a little iron powder or iodine as a carrier until the correct increase in weight is obtained. The liquid is then poured into water, washed with alkali, separated, dried and distilled. It may also be prepared by the diazo reaction. It is a colourless liquid boiling at 132°, is denser than water and possesses a pleasant aromatic odour.

**Bromobenzene,** $C_6H_5Br$, is prepared in a similar way, using the theoretical amount of bromine. It boils at 155°.

**Iodobenzene,** $C_6H_5I$, can only be prepared by the diazo reaction (p. 58). It is a colourless liquid boiling at 188°.

*o*-**Chlorotoluene** is a liquid possessing all the usual properties of a nuclear halogen derivative of the benzene series. It boils at 157°. It is formed together with the para isomeride when cold toluene is treated with chlorine in the presence of a carrier such as iodine or iron powder. It is best prepared in the pure state by the diazo reaction from pure *o*-toluidine. On oxidation with potassium permanganate it yields *o*-chlorobenzoic acid.

*m*-**Chlorotoluene** cannot be prepared directly from toluene (cf. Crum Brown and Gibson's rule). It is best prepared from *p*-toluidine (p. 48) by the following series of reactions:




*p*-**Chlorotoluene** is prepared (mixed with the ortho compound) by direct chlorination of toluene in the cold with a carrier. The pure substance is prepared by the diazo reaction from *p*-toluidine. It boils at 156°. On oxidation it yields *p*-chlorobenzoic acid.

**Benzyl chloride,** $C_6H_5CH_2Cl$, is isomeric with the chloro-

toluenes, but possesses entirely different properties. It is prepared by passing dry chlorine into a weighed amount of boiling toluene under reflux until the theoretical increase of weight has been obtained. The product is then fractionally distilled. The reaction takes place more rapidly in **bright sunlight.**

Benzyl chloride is a colourless liquid insoluble in water and boiling at 175°. It has a pungent smell and the liquid and vapour are extremely irritating to the skin and eyes. In its reactions it resembles the alkyl halides. Thus boiling alkalis produce hydrolysis with the formation of benzyl alcohol, $C_6H_5CH_2OH$. With silver nitrite it yields **phenyl nitromethane,** $C_6H_5CH_2NO_2$, with ammonia **benzylamine,** $C_6H_5CH_2NH_2$, and with potassium cyanide, **benzyl cyanide,** $C_6H_5CH_2CN$. On oxidation with aqueous copper nitrate it yields **benzaldehyde,** and with dilute nitric acid or potassium permanganate benzoic acid.

**Benzal chloride,** $C_6H_5CHCl_2$, is prepared in the same way as benzyl chloride, but the chlorination is prolonged until twice as much chlorine has been absorbed. It may also be prepared by warming together benzaldehyde and phosphorus pentachloride:

$$C_6H_5CHO + PCl_5 = C_6H_5CHCl_2 + POCl_3$$

In both cases the pure product is isolated by fractional distillation. Benzal chloride is a colourless liquid insoluble in water and boiling at 205°. When heated with dilute alkalis it is hydrolysed to benzaldehyde:

$$C_6H_5CHCl_2 + H_2O = C_6H_5CHO + 2\,HCl$$

Benzaldehyde is made commercially by heating benzal chloride (prepared from toluene) with milk of lime under pressure.

**Benzotrichloride,** $C_6H_5C \cdot Cl_3$, is the final chlorination product of boiling toluene. It is a liquid boiling at 213° with the irritating odour characteristic of aromatic side chain halides. When heated with alkalis, such as milk of lime, under pressure it is hydrolysed to benzoic acid. The first step in the hydrolysis is probably the formation of $C_6H_5 \cdot C(OH)_3$, but as (with very few exceptions, such as chloral hydrate) compounds in which more

than one hydroxyl group is attached to the same carbon atom are unstable, immediately losing water, this "ortho" benzoic acid immediately breaks down, forming $C_6H_5COOH$.

### Derivatives of Iodobenzene

**Phenyliodide-dichloride,** $C_6H_5ICl_2$, is a yellow solid produced when chlorine is passed into a chloroform solution of iodobenzene.

**Iodosobenzene,** $C_6H_5IO$, is produced when phenyliodide-dichloride is shaken with caustic potash: $C_6H_5ICl_2 + 2\ KOH = C_6H_5IO + 2\ KCl + H_2O$. It is an amorphous solid which explodes on heating and possesses oxidising properties, liberating two atoms of iodine from potassium iodide. When gently heated or boiled with water it undergoes auto-oxidation and reduction, forming phenyliodide and iodoxybenzene, $2\ C_6H_5IO = C_6H_5I + C_6H_5IO_2$.

**Iodoxybenzene,** $C_6H_5IO_2$, is an explosive solid and a powerful oxidising agent.

**Diphenyliodonium hydroxide,** $(C_6H_5)_2I.OH$, is produced when a mixture of iodosobenzene and iodoxybenzene is shaken with moist silver oxide:

$$C_6H_5IO + C_6H_5IO_2 + AgOH = (C_6H_5)_2IOH + AgIO_3$$

Diphenyliodonium hydroxide has not been isolated from its aqueous solution. It is a powerful base, the solution being strongly alkaline and absorbing carbon dioxide from the air. It yields a large number of well-defined crystalline salts, of which the halides and chromate are sparingly soluble.

Its salts show a remarkable resemblance in colour and solubility to the corresponding thallium compounds.

## CHAPTER V

## SULPHONIC ACIDS

ALL aromatic compounds react with hot concentrated sulphuric acid, forming sulphonic acids:

$$C_6H_5 . H + HO . SO_3H = C_6H_5SO_3H + H_2O$$

Benzene sulphonic acid

It will be remembered that this reaction is characteristic of the aromatic series and has no parallel among the aliphatic compounds, sulphonic acids of which can only be prepared by oxidising the mercaptans.

If fuming sulphuric acid is employed *meta* disulphonic acids are usually formed, and on very prolonged action three sulphonic acid groups may be introduced. Occasionally chlorosulphonic acid is employed, but this is usually too violent a reagent and gives very impure products:

$$C_6H_6 + ClSO_3H = C_6H_5SO_3H + HCl$$

**Benzene sulphonic acid**, $C_6H_5SO_3H$. This is prepared by heating benzene with excess of concentrated sulphuric acid (or better, slightly fuming acid) in a flask fitted with a reflux condenser. The hydrocarbon slowly dissolves, the rate of solution being accelerated by frequent shaking. When the benzene has dissolved the reaction mixture may be worked up in two ways.

(*a*) The acid mixture is poured into excess of strong brine, when the sodium benzene sulphonate formed crystallises out on cooling [*salting out* process].

(*b*) The sulphonation mixture is diluted, cooled and neutralised with chalk. The precipitated calcium sulphate is filtered off

and the solution of calcium benzene sulphonate mixed with sodium carbonate solution until all the calcium has been precipitated as carbonate. The solution is filtered and concentrated, when sodium benzene sulphonate crystallises.

To prepare the free acid the latter method is employed using barium carbonate. The barium salt is then decomposed with the theoretical amount of sulphuric acid, and the solution after filtration is evaporated to dryness.

The sulphonic acids in general are colourless solids readily soluble in water and frequently (as in the case of benzene sulphonic acid) very deliquescent. The salts of sulphonic acids are all easily soluble in water. The marked solubility of the sulphonic acids is of great technical value, for most dye stuffs are insoluble in water and could therefore only be applied in alcoholic solution. This difficulty is avoided by converting the dye stuff into its sulphonic acid (or preparing it from compounds containing sulphonic acid groups) whereby the shade is not appreciably altered but the dye can be applied in aqueous or alkaline solution. Indigo is frequently utilised in this way, the sulphonic acid being known commercially as "*indigo-carmine.*"

Sulphonic acids (with the exception of benzene sulphonic acid, which melts at 50°) decompose on heating, charring but not melting. When heated with water or **acids** under pressure the sulphonic acid group is removed:

$$C_6H_5SO_3H + H_2O = C_6H_6 + H_2SO_4$$

This process is employed in the separation of the xylenes (p. 18). When heated with **potassium cyanide** sulphonic acids are converted into the corresponding nitriles:

$$C_6H_5SO_3K + KCN = C_6H_5CN + K_2SO_3$$

Benzonitrile

This affords a simple method of introducing a carboxyl group into a benzene nucleus, since nitriles are readily hydrolysed to acids. When sulphonates are heated with **potassium formate** the **carboxyl** group is introduced directly:

$$C_6H_5SO_3K + H.COOK = C_6H_5.COOH + K_2SO_3$$

The most important property of the sulphonic acids, however,

is their reactivity towards potassium hydroxide. When a sulphonic acid is fused with **caustic potash** (soda cannot be used in this reaction) a **phenol** is obtained:

$$C_6H_5SO_3K + KOH = C_6H_5OH + K_2SO_3$$

This is one of the chief methods employed for the preparation of phenols.

When benzene sulphonic acid or one of its salts is treated with **phosphorus pentachloride** the corresponding acid chloride is formed and can be separated by fractional distillation under reduced pressure:

$$C_6H_5SO_3Na + PCl_5 = C_6H_5SO_2Cl + NaCl + POCl_3$$

**Benzene sulphonic chloride,** $C_6H_5SO_2Cl$, is a colourless liquid insoluble in water and boiling at 115° *in vacuo.* It decomposes on distillation under ordinary pressures. Though an acid chloride, it is practically unattacked by cold water. It possesses the usual chemical properties of an acid chloride. Thus with water it (very slowly) yields the acid, with alcohol an ester and with ammonia or amines, amides:

$$C_6H_5SO_2Cl + H_2O = \underset{\text{Benzene sulphonic acid}}{C_6H_5SO_2OH} + HCl$$

$$C_6H_5SO_2Cl + C_2H_5OH = \underset{\text{Ethylbenzene sulphonate}}{C_6H_5SO_2OC_2H_5} + HCl$$

$$C_6H_5SO_2Cl + NH_3 = \underset{\text{Benzene sulphonamide}}{C_6H_5SO_2NH_2} + HCl$$

$$C_6H_5SO_2Cl + C_6H_5NH_2 = \underset{\text{Benzene sulphonanilide}}{C_6H_5SO_2 . NHC_6H_5} + HCl$$

The derivatives obtained with amines are well defined crystalline substances of definite melting-point, and benzene sulphonic chloride is therefore sometimes used to characterise an unknown or impure amine. Conversely, many sulphonic acids which do not crystallise easily and have no definite melting-point, may be characterised by converting them into the acid chloride, treating this with ammonia or aniline and determining the melting-point of the resulting sulphonamide.

**Benzenesulphonamide,** $C_6H_5SO_2NH_2$, prepared by grinding together benzene sulphonic chloride and ammonium carbonate and extracting the product with water, is a white crystalline solid melting at 150°.

Substances of the type $C_6H_5SO_2NH_2$ or $C_6H_5SO_2NHR$ are soluble in caustic alkalis and therefore probably possess the structure $C_6H_5-S(=O)(=NH)-OH$ or $C_6H_5-S(=O)(=NR)-OH$.

This property affords a method of distinguishing between primary, secondary, and tertiary amines.

Primary amines with benzene sulphonic chloride give sulphonamides of the formula $C_6H_5SO_2NHR$, which dissolve in alkalis.

Secondary amines give sulphonamides of the type $C_6H_5SO_2NRR'$ where there is no possibility of a tautomeric hydroxylic structure and these compounds are insoluble in alkali.

Tertiary amines are of course nonreactive towards sulphonic chlorides.

**Benzene sulphinic acid,** $C_6H_5SO_2H$, is formed (as the zinc salt) when benzene sulphonic chloride is reduced with zinc dust. It possesses reducing properties and on further reduction with sodium amalgam yields **phenylmercaptan,** $C_6H_5SH$.

## CHAPTER VI

### NITRO COMPOUNDS

ONE of the important distinctions between aliphatic and aromatic compounds is based on the action of concentrated nitric acid on these substances. Whereas aliphatic compounds are usually oxidised (frequently with explosive violence) aromatic compounds yield nitro compounds, the nitro group entering the benzene ring. The nitro compounds are important because they form the link between the hydrocarbons and the amines. From the amines many aromatic substances may be readily synthesised owing to the great reactivity of the amino group. Nitro compounds are also used as yellow **dye stuffs** (cf. Naphthol yellow, p. 116) and form the basis of many **explosives**, such as lyddite (tri-nitrophenol, picric acid).

The actual details of the nitration depend on the substance to be nitrated and the number of nitro groups to be introduced.

Hydrocarbons are usually nitrated by slowly adding to them a mixture of concentrated nitric and sulphuric acids with external cooling, finally warming for a short time and then pouring the mixture into water or on to crushed ice. If a polynitro derivative is required a large excess of sulphuric acid, fuming nitric acid and a higher temperature are employed. The sulphuric acid acts as a dehydrating agent, combining with the water produced. Not more than three nitro groups can be introduced by direct nitration.

The presence of a hydroxyl group greatly increases the susceptibility of the benzene nucleus, and therefore to obtain mononitrophenols cold dilute nitric acid must be used.

Amines cannot be nitrated directly, since oxidation of the

benzene ring results. They must first be **acetylated**, the acetyl compound nitrated and finally the acetyl group removed by hydrolysis with hydrochloric acid. One of the best ways of preparing nitro compounds in general consists in dissolving the substance in strong sulphuric acid, slowly adding (with careful cooling) the theoretical amount of powdered nitre, allowing to stand for some hours and finally pouring the mixture on to crushed ice. If a very large excess of sulphuric acid is used even amines may be directly nitrated with concentrated nitric acid.

The nitro compounds are yellow solids (or in a few cases liquids) insoluble in water. The colour is usually intensified by alkali. The mononitrohydrocarbons possess a strong almond odour and nitrobenzene is used as a flavouring essence on this account. The mononitrohydrocarbons distil unchanged, but all other nitro compounds decompose on heating, frequently with a slight explosion or deflagration accompanied by the evolution of thick black fumes.

Nitro compounds are identified by their yellow colour, which is intensified by alkalis, by the violent deflagration accompanied by black fumes on heating with sodium, and by reduction with stannous chloride to the corresponding amine which is characterised by the carbylamine reaction (with chloroform and caustic soda) or by the preparation of an azo colour (p. 152). If necessary the amine may be extracted from the reduction mixture by adding alkali and extracting with ether. Amines are usually obtained by acid reduction. If neutral or alkaline reducing agents are employed other products are generally formed.

If polynitrohydrocarbons are treated with caustic potash and potassium ferricyanide they are oxidised to nitrophenols. Thus *m*-dinitrobenzene yields 2.4 dinitrophenol and 1.3.5 trinitrobenzene yields picric acid.

**Nitrobenzene**, $C_6H_5NO_2$, is prepared by adding to one part of benzene a cooled mixture of two parts of concentrated nitric acid and three of concentrated sulphuric acid. The solution must be kept below 30° during the addition of the acid or

dinitrobenzene will be formed. When all the acid has been added the mixture is heated on the water bath for a few minutes with frequent shaking and poured into excess of water. The nitrobenzene is then separated, washed successively with caustic alkali and with water and finally dried over calcium chloride and distilled. As thus prepared it is a pale yellow poisonous liquid boiling at 206°, insoluble in and denser than water (sp. gr. 1·20). It possesses a powerful odour of almonds and in very dilute alcoholic solution is used under the name of "essence of mirbane" for flavouring.

*m*-**Dinitrobenzene**, $C_6H_4\begin{cases}NO_2\ (1)\\NO_2\ (3)\end{cases}$ is the only important dinitrobenzene and is prepared by nitrating benzene or nitrobenzene with a mixture of fuming nitric acid and sulphuric acid, using a considerably greater proportion of sulphuric acid than is necessary in preparing nitrobenzene and carrying out the reaction at 100° C. A little of the oily layer is from time to time poured into excess of cold water until it completely solidifies.

The acid mixture is then poured into water and the precipitated dinitrobenzene recrystallised from alcohol, in which it is fairly easily soluble. As thus prepared it forms very pale yellow odourless needles melting at 90° and boiling at 300° with considerable decomposition. On reduction with stannous chloride, iron or zinc and acetic or hydrochloric acid it yields

*m*-**phenylenediamine**, $C_6H_4\begin{cases}NH_2\ (1)\\NH_2\ (3)\end{cases}$ which is used in the colour industry for making *Bismarck brown* and *Chrysoïdine*. If ammonium sulphide is used as the reducing agent only one nitro group is reduced to $NH_2$ (this is a general rule with polynitro compounds) and *m*-**nitraniline** is formed.

*Symm.* **Trinitrobenzene**, $C_6H_3\begin{cases}NO_2\ (1)\\—NO_2\ (3)\\NO_2\ (5)\end{cases}$ is formed with considerable difficulty when *m*-dinitrobenzene is heated for a long

time to a high temperature with a mixture of fuming nitric acid and a large excess of fuming sulphuric acid. It is a pale yellow solid melting at 121° and is oxidised by alkaline ferricyanide solution to picric acid.

*o*-**Nitrotoluene**, $C_6H_4\begin{cases}CH_3\ (1)\\NO_2\ (2)\end{cases}$ mixed with its para isomer is formed when toluene is nitrated under the same conditions as benzene. Since the ease of nitration is greater the more alkyl groups are present it is advisable to slightly decrease the amount of sulphuric acid used. The resulting mixture of nitro compounds is separated by fractional distillation. *o*-Nitrotoluene is a liquid resembling nitrobenzene in physical and chemical properties and boiling at 217°. On reduction it yields *o*-toluidine.

*m*-**Nitrotoluene** can only be prepared indirectly from *p*-toluidine.

The course of the preparation is exactly analogous to that described for *m*-chlorotoluene (p. 23), the acet-*p*-toluidide being nitrated instead of chlorinated.

*p*-**Nitrotoluene**, $C_6H_4\begin{cases}CH_3\ (1)\\NO_2\ (4)\end{cases}$ mixed with the ortho compound is formed when toluene is nitrated. It is separated by fractional distillation. It forms yellow crystals melting at 54°, boiling at 230° and possessing the usual odour of almonds. Mixed with ammonium nitrate it forms the basis of many *smokeless powders*.

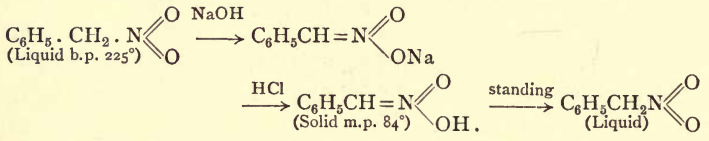
*Sym.* **Trinitro** *tert.* **butyl benzene** is prepared by strongly nitrating tertiary butyl benzene (made by the Friedel and Crafts' reaction from benzene and tertiary butyl chloride). It has a most powerful odour of musk and is used as a substitute for this substance.

The aromatic nitro compounds such as nitrobenzene, though they resemble the aliphatic nitro compounds in certain respects (*e.g.* by being reduced to amines with tin and hydrochloric acid), differ from them in being non-reactive to nitrous acid and also

in giving products other than amines with certain reducing agents.

A true aromatic analogue of nitromethane is

**Phenylnitromethane**, $C_6H_5CH_2NO_2$. This is made by heating benzyl bromide or iodide with silver nitrite, and possesses the characteristic properties of a nitroparaffin. It is a colourless oil boiling at 225° and the aqueous solution does not colour ferric chloride. It dissolves in caustic soda, giving a sodium salt which on decomposition with cold dilute acid precipitates an unstable form of phenylnitromethane as a crystalline solid melting at 84°. This solid is apparently a *hydroxy* compound since its solution gives a deep red colour with ferric chloride and it reacts with phosphorus pentachloride and with benzoyl chloride. On standing it soon changes into the stable liquid modification. The course of the reaction is probably as follows:




In the case of *m*-nitrophenylnitromethane the change has been followed by conductivity measurements. A solution of the sodium salt was treated with the theoretical amount of hydrochloric acid in a conductivity cell, and it was found that the conductivity of the solution slowly fell to the value due to the sodium chloride present as the ionised pseudo-acid slowly changed into the unionised nitro compound.

## CHAPTER VII

## REDUCTION PRODUCTS OF NITROBENZENE

NITRO compounds give rise to a number of compounds on reduction, according to the nature of the reducing agent.

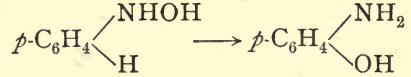
**A. Acid reducing agents.** Of these the chief are stannous chloride, tin or iron with hydrochloric acid, and iron or zinc dust with acetic acid. Under these conditions only amines are formed.

**B. Neutral reducing agents,** such as the aluminium-mercury couple with water and zinc dust or sodium amalgam with calcium chloride solution:

$$Al + 3\,H_2O = Al(OH)_3 + 3\,H$$
$$2\,Na + CaCl_2 + 2\,H_2O = 2\,NaCl + Ca(OH)_2 + 2\,H$$
$$Zn + 2\,H_2O = Zn(OH)_2 + 2\,H$$

Nitrobenzene under these conditions is reduced to

**Phenylhydroxylamine,** $C_6H_5NHOH$, which is extracted from the solution by ether. It is a colourless solid (m.p. 81°) and a powerful reducing agent. On warming with mineral acids it undergoes intramolecular rearrangement, yielding *p*-aminophenol:



It readily oxidises on exposure to air, forming **azoxybenzene,** $C_6H_5N{-}N.C_6H_5$, and on shaking with chromic acid mixture

it yields

**Nitrosobenzene,** $C_6H_5NO$, a white solid which melts to a blue liquid.

**C. Alkaline Reduction.** If nitrobenzene is boiled with a methyl alcoholic solution of sodium methoxide the latter is oxidised to sodium formate and on evaporating off the alcohol and extracting with ether azoxybenzene is obtained. A less pure product is obtained if alcoholic potash is used instead of sodium methoxide.

**Azoxybenzene,** $C_6H_5N-NC_6H_5$ (O bridging the two N), is a pale yellow solid melting at 36° and insoluble in water. When digested with strong sulphuric acid it undergoes intramolecular rearrangement, forming *p*-oxyazobenzene :

On acid reduction it gives aniline, $C_6H_5NH_2$.

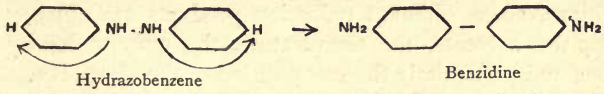
On distillation with iron filings, or when its alcoholic solution is boiled with caustic soda and zinc dust, azobenzene is formed.

**Azobenzene,** $C_6H_5 . N=N . C_6H_5$, is best prepared directly from nitrobenzene by boiling this for some hours with alcoholic potash (giving azoxybenzene) and then adding zinc dust and boiling for a further period. On pouring into acid the azobenzene is precipitated and may be purified by distillation or by recrystallisation from alcohol.

Azobenzene forms red plates melting at 68° and boiling at 293°. It is insoluble in water and very stable towards ordinary reagents. Like azoxybenzene it is reduced to aniline by stannous chloride, the double linking between the nitrogen atoms being broken. Reduction with zinc dust and acetic acid yields **hydrazobenzene.**

**Hydrazobenzene,** $C_6H_5NH . NHC_6H_5$, is a white crystalline solid melting at 131°. On exposure to the air it absorbs oxygen and turns red owing to the formation of azobenzene. Stannous chloride reduces it to aniline. The most important property of hydrazobenzene is the rearrangement it undergoes when warmed with strong hydrochloric acid, the molecule apparently breaking in half and recombining at the carbon atoms *para* to the nitrogen

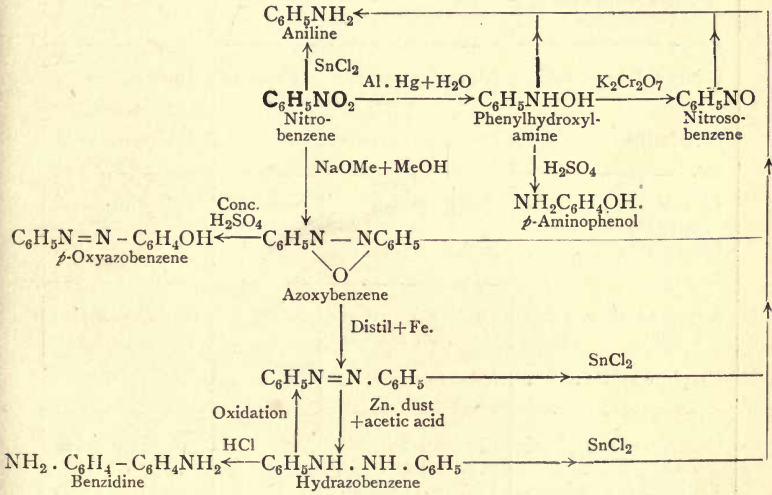
groups. The resulting substance is the hydrochloride of **benzidine** (*p.p.*-diaminodiphenyl) and the reaction is known as the **benzidine transformation:**




Hydrazobenzene — Benzidine

It is obvious that if the para positions of the hydrazo compound are substituted this reaction is impossible.

The relation between the various reduction products of nitrobenzene can be more clearly shown by the following table:




### Electrolytic Reduction of Nitrobenzene

Electrolytic processes for the reduction of nitro compounds have attained considerable importance within the last few years, since the yields are good, the products pure and the apparatus simple.

The method consists in electrolysing a solution of the nitro compound in a variety of solvents. As a rule a divided cell is used, the cathode and nitro compound being contained in a

porous pot. It is also advisable to stir the liquid rapidly, usually by rotating the cathode, which is mounted on a spindle.

The chief difficulty lies in determining the most suitable conditions, since different reduction products are obtained by varying the solvents, the temperature, the current density and voltage, and particularly the composition of the electrodes.

The following table shows the conditions for the formation of various products from nitrobenzene:

| Anode Compartment. | Cathode Compartment. | Current Density. | Product. |
|---|---|---|---|
| Dilute sulphuric acid.<br>Pure lead anode . | Alcohol + 30 per cent. sulphuric acid at 70° C.<br>Pure lead cathode | 5 amps. | Aniline. |
| 15 per cent. sodium sulphate solution<br>Lead anode . . | Caustic potash<br>Nickel cathode | 5 amps. | Azoxybenzene. |
| Saturated sodium carbonate<br>Graphite anode. . | 70 per cent. alcohol + sodium acetate<br>Nickel cathode | | Azobenzene. |
| Concentrated sulphuric acid<br>Platinum anode . | Concentrated sulphuric acid<br>Platinum cathode | | *p*-Aminophenol. |

In the last case phenylhydroxylamine is first produced and is rearranged under the influence of the concentrated acid.

## CHAPTER VIII

### AMINES

THE aromatic amines (or *amido compounds* as they are sometimes termed, since they possess several properties without analogy among the aliphatic amines) correspond in type with the aliphatic amines. They may be considered as ammonia with one or more hydrogen atoms replaced by aryl groups, or as aromatic substances in which nuclear hydrogen atoms are replaced by the groups $NH_2$, NHR, etc.

Primary amines are almost invariably prepared by the reduction of nitro compounds in acid solution. In the laboratory the usual reducing agent is tin or stannous chloride and hydrochloric acid. On a commercial scale the expensive tin is replaced by iron filings. Other reducing agents frequently used are iron powder and hydrochloric acid, zinc dust and acetic acid and sometimes alcoholic ammonium sulphide.

Less common methods of preparation occasionally used are:

(1) Reducing an azo compound with stannous chloride. This is a useful method for preparing aminophenols or diamines.

(2) Heating the corresponding phenol under pressure with the compounds calcium chloride-ammonia or zinc chloride-ammonia. This method is usually adopted in the naphthalene series.

Aromatic amines cannot be prepared by heating the corresponding halides, *e.g.* bromobenzene, with ammonia as the halogen is too firmly held by the benzene nucleus.

Ammonium sulphide is generally used when it is required partially to reduce a *poly*-nitro compound. Under these con-

ditions only one nitro group is reduced. Thus *m*-dinitrobenzene yields *m*-nitraniline. The simple amines are as a rule high boiling liquids or easily fusible solids, which distil without decomposition. They have a characteristic basic odour, are insoluble in water and gradually darken on exposure to air. The tendency to oxidise is very marked when two or more amino groups are present in the benzene ring.

As regards their chemical properties they are much **weaker bases** than the corresponding aliphatic amines. The phenyl group appears to possess a slight acidic nature, for diphenylamine $(C_6H_5)_2NH$ is a very weak base while triphenylamine $(C_6H_5)_3N$ possesses no basic properties. This acidic nature is also shown in the case of the phenols, which, unlike the hydroxy derivatives of the paraffins, behave as weak acids. The amines (with the exception of triphenylamine) are soluble in dilute acids and on concentration of the solutions the corresponding salts crystallise out. The nitrates and hydrochlorides are readily soluble, the sulphates less soluble and the platinichlorides sparingly so. Stannichlorides and addition compounds with calcium chloride analogous to the corresponding ammonia compounds are also readily formed. For this reason amines cannot be dried with calcium chloride. Caustic potash should be used. The salts differ from those of the aliphatic amines in being considerably **hydrolysed by water** and therefore possessing an acid reaction. The amount of acid thus set free can be completely titrated with caustic alkali, using phenol-phthalein, and thus affords a ready method of determining the equivalent weight of the amine. The hydrochlorides are frequently employed for this purpose and for preparation work are best made by the following methods:

(1) Grind the amine with a little more than the theoretical amount of concentrated hydrochloric acid in a mortar and dry the product on porous tile.

(2) Mix alcoholic solutions of the amine and of hydrogen chloride and add ether, when the hydrochloride is precipitated. Salts prepared by the first method may frequently be purified by solution in alcohol and precipitation by ether.

(3) Dissolve the amine in benzene or ether and pass in dry hydrogen chloride when the hydrochloride is precipitated.

When heated with alkyl halides under pressure the aromatic amines undergo the same changes as the aliphatic amines. Thus:

$$C_6H_5NH_2 \xrightarrow{CH_3I} C_6H_5NHCH_3 \longrightarrow C_6H_5N(CH_3)_2 \longrightarrow C_6H_5N(CH_3)_3I$$

secondary and tertiary amines and finally a quaternary ammonium salt being produced. If the secondary and tertiary amines are heated more strongly (usually to 300°) the **alkyl group migrates into the ring.**

Thus methylaniline, $C_6H_5NHMe$, is converted into toluidine, $C_6H_4Me.NH_2$, a mixture of *ortho* and *para* isomerides being obtained. Dimethylaniline, $C_6H_5NMe_2$, in the same way gives firstly a methyltoluidine, $C_6H_4Me.NHMe$, and finally a xylidine (amino xylene), $C_6H_3Me_2.NH_2$.

### Primary Amines

The primary amines are usually prepared by reduction of the corresponding nitro compound with tin or iron and hydrochloric acid. The majority are liquids boiling above 180°, insoluble in water, possessing a basic odour and giving rise to a series of salts. They are colourless when pure, but become brown on standing. This tendency is far more marked in the case of the diamines than with the monamines. It is practically impossible to obtain the former in a colourless condition. The *presence of the amino group makes the benzene ring much more sensitive towards reagents.* Thus aniline reacts immediately with chlorine or bromine, yielding the symmetrical tri-halogen compound. Primary amines cannot be directly nitrated as complete decomposition ensues. To prepare a nitro- or a mono-halogen derivative of an amine it is first necessary to acetylate this to "protect" the amino group. The acetyl compound may now be nitrated or brominated in the usual way, the product isolated and the substituted amine finally prepared by hydrolysis of the acetyl compound. The primary amines undergo the following characteristic reactions:

(1) When heated with acetic anhydride, acetyl chloride or

sometimes even with acetic acid they yield acetyl derivatives. These are solids which crystallise well and are frequently used for characterising the amines:

$$\underset{\text{Aniline}}{C_6H_5NH_2} + (CH_3CO)_2O = \underset{\text{Acetanilide}}{C_6H_5NHCOCH_3} + CH_3COOH$$

If benzoyl chloride is used (*see Schotten-Baumann reaction*) a benzoyl derivative is obtained. These derivatives are known as "anilides" when prepared from aniline, "toluidides" when prepared from toluidines, etc. Being substituted amides they are hydrolysed by boiling acid or alkalis (best by concentrated hydrochloric acid) to the corresponding acid and amine.

(2) When dissolved in acid and treated with ice-cold nitrous acid diazo compounds are obtained (p. 56):

$$C_6H_5NH_2 + O:N.OH + HCl = \underset{\text{Diazobenzene chloride}}{C_6H_5N:N.Cl} + 2\,H_2O$$

These are unstable and on warming decompose into the corresponding phenol and nitrogen:

$$C_6H_5N_2Cl + HOH = \underset{\text{Phenol}}{C_6H_5OH} + N_2 + HCl$$

In hot solution, therefore, aromatic primary amines behave like their aliphatic analogues, but differ from them in giving an intermediate product in cold solution.

(3) When heated with carbon disulphide and a trace of sulphur as catalyst substituted **thioureas** are formed:

$$SCS + \begin{matrix} H\,NHC_6H_5 \\ H\,NHC_6H_5 \end{matrix} = \underset{\text{Thiocarbanilide or diphenylthiourea}}{SC\begin{matrix} NHC_6H_5 \\ NHC_6H_5 \end{matrix}} + H_2S$$

(4) When warmed with alkali and a drop of chloroform the isonitrile, recognisable by its offensive odour, is produced:

$$C_6H_5NH_2 + CHCl_3 = C_6H_5NC + 3\,HCl$$

(5) When warmed with sodium substituted sodamides are formed:

$$2\,C_6H_5NH_2 + 2\,Na = 2\,C_6H_5NHNa + H_2$$

These substances are very unstable, being immediately decomposed by moisture.

(6) Primary amines condense with aromatic aldehydes in alcoholic solution, giving well-defined crystalline products:

$$\underset{\text{Aniline}}{C_6H_5NH_2} + O{:}HC\,.\,\underset{\text{Benzaldehyde}}{C_6H_5} = \underset{\text{Benzylideneaniline}}{C_6H_5N:CHC_6H_5} + H_2O$$

**Aniline**, $C_6H_5NH_2$. This is the simplest and most important of the aromatic amines. The name is derived from the Portuguese (*anil* = indigo), since it was first obtained by the destructive distillation of indigo (Unverdorben, 1826). It is now prepared by the reduction of nitrobenzene. In the laboratory this is carried out by adding nitrobenzene to a warm hydrochloric acid solution of stannous chloride or by adding strong hydrochloric acid to a mixture of tin and nitrobenzene (using a slight excess of the reducing agent). Considerable heat is evolved, the odour of nitrobenzene disappears and the whole mass sets to a crystalline paste of *aniline stannichloride*, $(C_6H_5NH_2)_2H_2SnCl_6$ (cf. ammonium stannichloride, $(NH_4)_2SnCl_6$). This is decomposed by adding excess of alkali and the aniline is distilled off in steam. The heavy oil (aniline) is separated from the distillate (or extracted with ether), dried with caustic potash and redistilled.

On a commercial scale the tin and hydrochloric acid are replaced by iron turnings and a very small amount of hydrochloric acid:

$$Fe + 2\,HCl = FeCl_2 + 2\,H$$
$$FeCl_2 + 3\,H_2O = Fe(OH)_3 + H + 2\,HCl\,.$$
$$2\,Fe(OH)_3 + Fe = 3\,Fe(OH)_2$$

When the action is over lime is added and the aniline distilled in steam. Since aniline is slightly soluble in water the aqueous portion of the distillate is used for feeding the boilers supplying the steam.

Aniline is a colourless liquid of sp. gr. 1·02 and boiling at 184°. It is only slightly soluble in water (3 per cent.), is poisonous, possesses a faint basic odour, and soon turns brown on exposure to air and light.

It is readily soluble in acids forming salts which can be

crystallised. They are best prepared pure by mixing alcoholic solutions of aniline and the acid and precipitating with ether.

The hydrochloride is readily soluble in water and forms white plates which hydrolyse when dissolved in water (and therefore possess an acid reaction) and which acquire a faint green colour on keeping. The sulphate is sparingly soluble and the platinichloride insoluble in water.

Aniline possesses the previously mentioned characteristic reactions of its class.

It may be detected by the purple colour produced when a trace of aniline (an aqueous solution should be used) is treated with bleaching powder solution.

**Acetanilide** (antifebrin), $C_6H_5NH.COCH_3$, is formed when aniline is heated with acetic anhydride for a few minutes or with acetic acid for a day. It is a white crystalline solid (m.p. 113°), soluble in boiling water, and is the chief constituent of most headache powders.

**Benzanilide** is best prepared by shaking together in caustic soda suspension equimolecular proportions of aniline and benzoyl chloride (the Schotten-Baumann reaction). It is a white solid melting at 163°. Other anilides can be prepared, using similar methods.

**Thiocarbanilide,** $SC(NHC_6H_5)_2$

This substance is produced when carbon disulphide and aniline in alcoholic solution are boiled together for several hours. The reaction is greatly accelerated by the presence of a trace of sulphur:

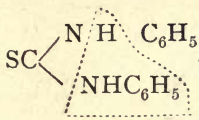
$$SC{:}S + \begin{matrix} H\,NHC_6H_5 \\ H\,NHC_6H_5 \end{matrix} = SC(NHC_6H_5)_2 + H_2S$$

Thiocarbanilide

When the reaction is complete the alcohol and excess of carbon disulphide are distilled off and the residual thiocarbanilide washed with dilute acid to remove aniline and recrystallised from hot alcohol. It forms white plates melting at 152°.

It is of importance as the source of **phenyl mustard oil.**

**Phenyl mustard oil,** phenyl isothiocyanate, $C_9H_5NCS$, is formed when thiocarbanilide is boiled for an hour with strong hydrochloric acid:




$$+ HCl = C_6H_5NCS + C_6H_5NH_2 . HCl$$

It is isolated from the reaction mixture by steam distillation.

It is a colourless oil boiling at 222°, and possessing a characteristic mustard-like odour. It is highly reactive and is frequently used to characterise amines, with which it readily combines to give well-defined crystalline derivatives of thiourea:

$$C_6H_5NCS + NH_3 = C_6H_5NHCSNH_2 \text{ (Phenylthiourea)}$$
$$C_6H_5NCS + C_6H_5NH_2 = C_6H_5NHCS . NHC_6H_5$$
(Diphenylthiourea or thiocarbanilide)

On distillation with yellow mercuric oxide it yields **phenyl isocyanate** or phenyl carbimide, which is used also for characterising amines and alcohols:

$$C_6H_5NCS + HgO = C_6H_5NCO + HgS$$
$$C_6H_5NCO + NH_2R = C_6H_5NH . CO . NHR \text{ (a phenyl urea)}$$
$$C_6H_5NCO + HO . R = C_6H_5NH . CO . OR \text{ (a phenyl urethane)}$$

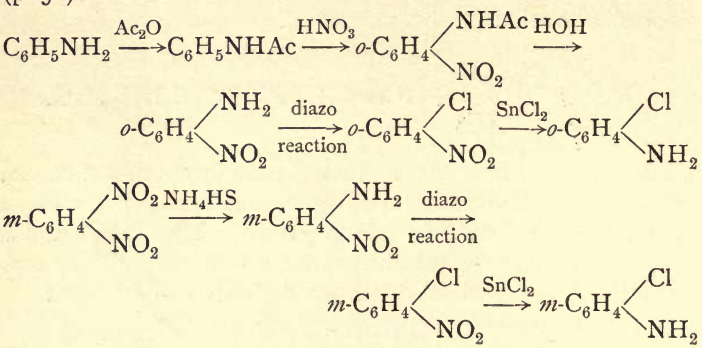
**Halogen Compounds.**—Aniline reacts immediately with the halogens, giving precipitates of the insoluble tri-substituted compounds. The mono-derivatives can only be made from acetanilide, in which the highly reactive amino group is "protected."

Acetanilide in acetic acid solution reacts with halogens, giving a mixture of ortho and para derivatives in which the para compound largely predominates. It has been shown that the first step in the reaction is the formation of an unstable derivative of nitrogen chloride:

$$C_6H_5NHCOCH_3 + Cl_2 = C_6H_5NCl . COCH_3 + HCl$$

The halogen atom readily wanders into the ortho or para position, forming haloid acetanilides which on hydrolysis with strong hydrochloric acid regenerate the corresponding amines.

Ortho and meta chloraniline are prepared indirectly from the corresponding nitro anilines by means of the diazo reaction (p. 58):


C6H5NH2 Ac2O C6H5NHAc HNO3 o-C6H4 NHAc NO2 HOH
o-C6H4 NH2 NO2 diazo reaction o-C6H4 Cl NO2 SnCl2 o-C6H4 Cl NH2
m-C6H4 NO2 NO2 NH4HS m-C6H4 NH2 NO2 diazo reaction
m-C6H4 Cl NO2 SnCl2 m-C6H4 Cl NH2

Ortho and meta chloranilines are liquids while the para compound is solid.

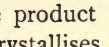
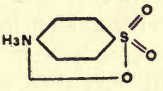
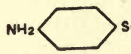
*Sym.* **Tribromaniline** is formed with extreme ease when bromine is brought into contact with aniline. It is a white crystalline solid (m.p. 119°) and quite insoluble in water, a fact which makes it a useful test for aniline, although most amines and phenols give a similar reaction. Then why is it a good test?

The presence of the two bromine atoms adjacent to the $NH_2$ group appears to hinder the latter from exerting its usual functions. Thus tribromaniline is not soluble in acids and cannot be diazotised by ordinary means. (See Chapter XX., "Steric Hindrance," p. 136.)

### Sulphonic Acids

Only two sulphonic acids of aniline are of importance, since these are used in the azo-dye industry.

**Metanilic acid,** aniline *m*-sulphonic acid, is a white infusible solid sparingly soluble in water. It is soluble in alkalis but not in acids, the acid nature of the sulphonic group overcoming the basic nature of the amido group. It cannot be made from aniline (cf. Crum Brown and Gibson's Rule) and is prepared by sulphonating nitrobenzene and reducing the product.

**Sulphanilic acid**, aniline *p*-sulphonic acid, is of great technical importance. It is prepared by heating aniline with excess of strong sulphuric acid at 190° until a test sample is completely soluble in caustic soda. The product is then poured into water, when the sulphanilic acid crystallises on cooling with $IH_2O$. Though usually written as  the free acid is probably an internal salt of the structure  since it gives no acetyl derivative and therefore probably does not contain the free $NH_2$ grouping. The sodium salt, however, has the formula  since this can readily be acetylated. Sulphanilic acid behaves abnormally on fusion with potash, aniline, and not *p*-aminophenol, being produced.

### Nitro Compounds

Aniline cannot be directly nitrated under ordinary conditions as this treatment produces complete decomposition. If, however, it is dissolved in sixty times its weight of strong sulphuric acid and the theoretical amount of potassium nitrate added, a good yield of *m*-nitraniline is produced on pouring the product on to ice. This affords an important exception to Crum Brown and Gibson's Rule.

*o*- and *p*-Nitranilines are made by adding acetanilide to cold fuming nitric acid. After some hours the solution is poured on to ice and the mixture of *o*- and *p*-nitracetanilides filtered off, dried and separated by extraction with chloroform, in which the para compound (which predominates in the mixture) is insoluble. Hydrolysis by means of boiling hydrochloric acid yields the free nitranilines.

***o*-Nitraniline** is a bright reddish-yellow solid melting at 71° C.

***p*-Nitraniline** forms pale yellow prisms melting at 147° C. It is largely used for the production of *p-Nitraniline Red* (p. 65).

*m*-**Nitraniline** may be made by the method described above or by the partial reduction of *m*-dinitrobenzene by means of warm ammonium sulphide. It is a yellow solid melting at 115°.

The nitranilines which contain the acidic nitro group are very feebly basic. The hydrochlorides are colourless. On further reduction by means of stannous chloride the three phenylene diamines are produced.

The amino derivatives of toluene are known as **Toluidines.** They closely resemble aniline in physical and chemical properties, the chief difference lying in the odour, which is more powerful and unpleasant than that of aniline; *p*-toluidine is a white crystalline solid. The toluidines occur in aniline which has been prepared from benzene containing toluene and they are largely used in the colour industry. Ortho and para toluidine are prepared in the same way as aniline, by acid reduction of the nitro compounds. A mixture of these compounds (in the form of their hydrochlorides) is produced by molecular rearrangement when methylaniline hydrochloride, $C_6H_5NHCH_3 . HCl$ (p. 51) is heated to 300°.

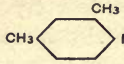
*o*-**Toluidine,** prepared by the reduction of *o*-nitrotoluene, is a liquid closely resembling aniline and boiling at 198°.

*m*-**Toluidine** cannot be prepared directly (cf. Crum Brown and Gibson's Rule). It is obtained by the reduction, with zinc dust and acid, of *m*-nitrobenzal chloride (from benzaldehyde by nitration and treatment with phosphorus pentachloride). It is a liquid boiling at 199°.

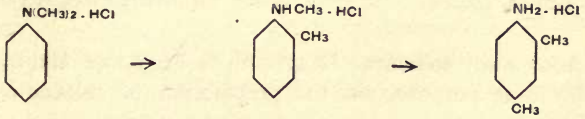
*p*-**Toluidine** is prepared by the reduction of *p*-nitrotoluene. It is the only common monamino-derivative of a benzenoid hydrocarbon which is solid at ordinary temperatures. It forms white plates possessing an unpleasant odour, melting at 44° and boiling at 198°.

The **acet-toluidides** closely resemble acetanilide in properties and method of preparation. They melt at 110°, 66° and 53° respectively.

**Xylidine.**—This name is applied to the mixture of amino xylenes obtained by the reduction of the nitration product of crude xylene.

The chief constituent is  which is also pre-

pared technically by **heating dimethylaniline hydrochloride** to a high temperature (300°):



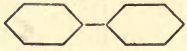
**Diamines.**—These substances are prepared by the reduction of dinitro or nitro-amino compounds. Those derived from benzene are known as *phenylene diamines* (the group $C_6H_4$ being termed "phenylene") and those from toluene *toluylene diamines.*

They possess similar properties to the monamines, only to a more marked extent. Thus they are **more reactive**, and darken so readily in the air that it is almost impossible to prepare colourless specimens. They are generally used in the form of their hydrochlorides, which are more stable.

*o*-**Phenylene diamine** is prepared by the acid reduction of *o*-nitraniline. It is a colourless solid when pure.

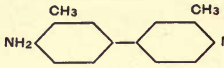
*m*-**Phenylene diamine** is prepared by the reduction of *m*-dinitrobenzene. It is used to a large extent in the colour industry for the preparation of Bismarck Brown (p. 65) and is also used as a test for traces of nitrous acid, with which it reacts to give this brown colouring matter.

*p*-**Phenylene diamine** is prepared by the reduction of *p*-nitraniline. It is used in the dye industry.

**Benzidine,**  diparadiaminodiphenyl,

is of great importance in the azo colour industry (p. 66) since the dyestuffs produced from it are "**substantive**," *i.e.* will dye cotton without a mordant. The preparation has been described in the previous chapter (p. 37). It depends on the intramolecular change produced when hydrazobenzene is heated with hydrochloric acid.

Benzidine is a colourless crystalline solid melting at 122°. It is readily soluble in hydrochloric acid but its sulphate is very sparingly soluble and affords a ready means of purifying the crude base.

**Tolidine,**  is prepared in an analogous way from *o*-nitrotoluene. It resembles benzidine and is used for the same purpose, viz. the preparation of substantive azo colours.

### Secondary Amines

Mixed aliphatic-aromatic amines (such as methylaniline, $C_6H_5NHCH_3$) are best prepared by heating the corresponding primary amine with an alkyl halide under pressure, $RNH_2 + R'Cl = RNHR' + HCl$. Purely aromatic secondary amines are prepared by heating together under pressure one primary amine with the hydrochloride of another. Thus diphenylamine is made from aniline and aniline hydrochloride, and phenylnaphthylamine from aniline and naphthylamine hydrochloride:

$$C_6H_5NH_2 . HCl + HNHC_6H_5 = (C_6H_5)_2NH + NH_4Cl$$

$$C_{10}H_7NH_2 . HCl + HNHC_6H_5 = C_{10}H_7NHC_6H_5 + NH_4Cl$$

Naphthylamine hydrochloride

The secondary aromatic amines are liquids or solids of low melting-point, insoluble in water but soluble in acids yielding crystallisable salts. They possess the basic odour of the primary amines, but in addition to this a faint, unpleasant fishy odour. Their reactions resemble those of their aliphatic analogues, the reaction with nitrous acid being most characteristic.

(1) They react with acetic anhydride, giving well-defined crystalline acetyl derivatives:

$$C_6H_5NHCH_3 + (CH_3CO)_2O =$$

Methylaniline

$$C_6H_5N(CH_3)COCH_3 + CH_3COOH$$

(2) On adding sodium nitrite to an acid solution a yellow oily **nitrosamine** is precipitated:

$$C_6H_5N(CH_3)H + HONO = C_6H_5(CH_3)N.NO$$

Nitrosomethylaniline

They differ from the primary amines in giving no diazo compound, no isocyanide reaction and no condensation products with aldehydes or carbon disulphide.

**Methylaniline**, $C_6H_5NHCH_3$, is found when aniline is heated with methyl iodide or sulphate. It is prepared technically by heating to 200° under pressure a mixture of aniline hydrochloride and methyl alcohol. These probably react to give aniline, water and methyl chloride, the methyl chloride then reacting with the aniline. At the same time a certain amount is further methylated, yielding dimethylaniline.

The reaction mixture is made alkaline, and the crude methylaniline separated. To free this from dimethylaniline it is digested with acetic anhydride when the secondary amine is acetylated, while dimethylaniline, being a tertiary amine, yields no acetyl derivative. On distillation acetic anhydride, acetic acid and dimethylaniline pass over, leaving the high boiling acetylmethylaniline, which may be hydrolysed with hydrochloric acid, to regenerate the base.

Methylaniline is a colourless liquid slightly lighter than water and boiling at 192°. Of its salts only the hydrochloride and platinichloride can be easily isolated. The nitrosamine is a yellow oil.

When methylaniline hydrochloride is heated to 300° the methyl group migrates into the ring and *o*- and *p*-toluidines are formed.

**Acetylmethylaniline** is used in medicine under the name of *exalgin*. It forms white prisms, more soluble in water than acetaniline, and melts at 101°.

**Ethylaniline**, $C_6H_5NHC_2H_5$, is prepared in a precisely similar way to methylaniline. It boils at 203° and its acetyl derivative melts at 54°.

**Diphenylamine**, $(C_6H_5)_2NH$, is prepared by heating aniline with aniline hydrochloride under pressure:

$$C_6H_5NH_2.HCl + HNHC_6H_5 = (C_6H_5)_2NH + NH_4Cl$$

Diphenylamine crystallises in colourless plates melting at 54° and boiling at 305°. It possesses an unpleasant odour and dissolves in acids. Owing to the presence of two phenyl groups (which possess acidic properties) diphenylamine is a much weaker base than aniline, which is itself much weaker than ammonia or the aliphatic amines. Diphenylamine is characterised by the intense blue colour produced when its solution in strong sulphuric acid is treated with a trace of nitrous or nitric acids. So delicate is this test that most specimens of sulphuric acid (made by the lead chamber process) give the coloration immediately.

The nitrosamine is a yellow solid melting at 66° and the acetyl derivative melts at 103°.

### Tertiary Amines

The mixed alkyl-aryl amines are prepared in the same way as the secondary amines, only the reaction is prolonged to complete the alkylation. They are used to a large extent in the colour industry.

The purely aromatic tertiary amines are of theoretical interest since the acidic nature of the phenyl groups is sufficiently marked so to overcome the basic characteristics of an ammonia derivative, that triphenylamine, for example, is a neutral substance.

The tertiary amines are, as one would expect from their formula, non-reactive towards acetic anhydride, carbon disulphide and chloroform.

The action with nitrous acid is, however, characteristic and important. Whereas the aliphatic tertiary amines are non-reactive towards nitrous acid, this reagent attacks the benzene ring of a tertiary aromatic amine **introducing a nitroso group** in the **para position.**

Thus: $C_6H_5N(CH_3)_2 + HONO = p\text{-}NO.C_6H_4.N(CH_3)_2 + H_2O$

*p*-Nitrosodimethylaniline

These *p*-nitroso compounds must not be confused with the true nitrosamines given by secondary amines. The former are **green basic solids** which on reduction yield derivatives of

*p*-diamines. Thus *p*-nitrosodimethylaniline yields dimethyl *p*-phenylenediamine.

The **true nitrosamines are yellow** neutral substances which on reduction yield substituted hydrazines:

$$\underset{\text{Nitrosomethylaniline}}{C_6H_5(CH_3)N \cdot NO} + 4H = \underset{\substack{\textit{unsym.}\ \text{Methylphenyl-}\\ \text{hydrazine}}}{C_6H_5(CH_3)N \cdot NH_2 \cdot} + H_2O$$

The aromatic tertiary amines, like their aliphatic analogues, combine directly with alkyl halides with evolution of heat, forming white crystalline alkyl-aryl quaternary ammonium salts:

$$C_6H_5N(CH_3)_2 + CH_3I = \underset{\substack{\text{Trimethylphenyl-}\\ \text{ammonium iodide}}}{C_6H_5(CH_3)_3NI}$$

**Dimethylaniline,** $C_6H_5N(CH_3)_2$, is prepared in the same way as methyl aniline, viz. by heating aniline hydrochloride with methyl alcohol under pressure, but the reaction is allowed to continue for a longer time at a higher temperature. The product is made alkaline, the oil separated and distilled with a small quantity of acetic anhydride, which retains any methylaniline as its acetyl derivative.

Dimethylaniline as thus prepared is a colourless liquid boiling at 192° and possessing a characteristic fishy basic odour. It is a stronger base than aniline and the salts are very soluble, only the hydrochloride being at all easily prepared; this is a white deliquescent solid.

Dimethylaniline unites directly with alkyl halides with evolution of heat, forming white crystalline quaternary ammonium salts.

The most characteristic reaction (which is common to all tertiary aromatic amines) is that obtained when an ice-cold acid solution is treated with sodium nitrite. The para position in the benzene ring is substituted and yellow needles of *p*-nitroso-dimethylaniline hydrochloride separate:

$$C_6H_5N(CH_3)_2 + HNO_2 + HCl = p\text{-}C_6H_4(NO)N(CH_3)_2 \cdot HCl$$

On treatment with cold alkali the free base is precipitated.

***p*-Nitrosodimethylaniline** crystallises in beautiful green leaflets melting at 85°. It is slightly soluble in water, giving a

yellow solution. It possesses a faint but characteristic odour and forms an addition compound with aniline which crystallises in magnificent blue needles. With hydrochloric acid it forms a yellow crystalline hydrochloride. It is hydrolysed by hot caustic alkalis, yielding dimethylamine and *p*-nitrosophenol. This is the best method for preparing dimethylamine:

$$p\text{-}C_6H_4\begin{cases}N(CH_3)_3\\NO\end{cases} + HOH = C_6H_4\begin{cases}OH\\NO\end{cases} + NH(CH_3)_2$$

*p*-Nitrosophenol

On reduction with stannous chloride *p*-nitrosodimethylaniline is converted into colourless dimethyl *p*-phenylene diamine:

$$p\text{-}C_6H_4\begin{cases}N(CH_3)_2\\NO\end{cases} + 4\,H = p\text{-}C_6H_4\begin{cases}N(CH_3)_2\\NH_2\end{cases} + H_2O$$

**Diethylaniline** is prepared in the same way as dimethylaniline and possesses similar physical and chemical properties. It boils at 213°.

### Primary Amines with the $NH_2$ Group in the Side Chain

These substances, the typical member being **benzylamine**, $C_6H_5CH_2NH_2$, differ as greatly from the nuclear amino compounds as benzyl chloride does from chlorobenzene, behaving like aliphatic amines just as benzyl chloride reacts in much the same way as an alkyl halide.

**Benzylamine**, $C_6H_5CH_2NH_2$, may be prepared by the following methods:

$$C_6H_5CH_2Cl + NH_3 \xrightarrow{\text{Sealed tube}} C_6H_5CH_2NH_2 + HCl$$

$$C_6H_5CN + 4\,H(\text{from Na + alc.}) = C_6H_5CH_2NH_2$$

$$C_6H_5CH{:}\,NOH + 4\,H(\text{from Na amalgam}) = C_6H_5CH_2NH_2 + H_2O$$

Benzaldoxime

In the first method (as in the analogous preparation of methylamine) di- and tribenzylamines are formed as a result of further reaction. Benzylamine behaves in all respects like an aliphatic amine. It is a liquid with a strong ammoniacal odour.

It dissolves in water, forming a strongly alkaline solution which absorbs carbon dioxide from the air and yields neutral salts with acids.*

**Nitrous acid reacts in the cold evolving nitrogen** and forming benzyl alcohol, no diazo compound being produced as with aniline.

* That is to say, the base is sufficiently strong to form salts which undergo no hydrolysis.

## CHAPTER IX

### DIAZO COMPOUNDS

IT has been previously mentioned that the aromatic primary amines, such as aniline, differ from the aliphatic primary amines in their reaction towards cold nitrous acid. The latter are immediately converted into alcohols while the aromatic compounds yield **diazo compounds.**

This reaction was discovered in 1860 by Griess, who investigated these compounds and showed their great value in synthetical chemistry.

The diazo compounds from aniline are salts of the monacid radicle $C_6H_5 . N : N—$ and are neutral crystalline solids.

The carbonate and hydroxide are strongly alkaline, hence this radicle is highly basic.

As a general rule the diazo compounds are prepared and used in aqueous solution as they are very soluble, but they rapidly decompose and when dry frequently explode.

The **solid diazonium salts** are prepared by dissolving a pure dry amine hydrochloride in ice-cold alcohol and adding the theoretical amount of **amyl nitrite.** This is hydrolysed by the hydrochloric acid and the nitrous acid produced *diazotises* the amine :

$$C_6H_5NH_2 . HCl + HNO_2 = C_6H_5N : NCl + H_2O$$

Diazobenzene chloride

After a few minutes the alcoholic solution is filtered into dry ether which precipitates the diazo salt. This can then be filtered and rapidly dried.

The diazonium salts readily decompose above 0° C., frequently with a violent explosion when dry.

**Solutions of diazonium salts** (the chloride is generally used) are prepared by dissolving the amine in excess of diluted hydrochloric acid, cooling in ice, and slowly adding a solution of the theoretical quantity of sodium nitrite. The following points must be borne in mind:

(1) *The colder the solution the better the yield.* As the reaction is exothermic cooling is necessary during the diazotisation.

When working on a small scale with most amines cooling under the tap will suffice, but better yields are obtained if lower temperatures are employed. *o*-Toluidine must be diazotised in ice to obtain a diazo solution free from tarry products.

(2) *A slight excess of acid must be present* or subsidiary reactions will go on. Though only two molecular proportions are theoretically necessary

$$(C_6H_5NH_2 + 2\,HCl + NaNO_2 = C_6H_5N{:}NCl + NaCl + 2\,H_2O)$$

not less than $2\frac{1}{2}$ mols. should be used. (100 c.c. of concentrated hydrochloric acid contain 36·5 grms. HCl.)

(3) *Excess of nitrous acid is harmful.* The solution may be tested with starch-iodide paper from time to time, or for ordinary purposes one can use the theoretical quantity of sodium nitrite (the commercial product almost invariably containing 96 per cent. of $NaNO_2$).

The following description of the preparation of a diazo solution may be taken as typical:

9·3 grms. (0·1 mol.) of aniline are mixed with 30 c.c. of water and 30 c.c. (0·3 mol.) of strong hydrochloric acid and crushed ice added until the solution is at 0° C. A cold solution of 7·1 (0·1 mol.) grms. of sodium nitrite (96 per cent.) in 15 c.c. of water is then added, drop by drop, with stirring and the occasional addition of ice. The solution turns slightly yellow and a little nitrogen is evolved. When all the nitrite is added the solution is allowed to stand for about two minutes to complete the reaction.

**Reactions of the Diazo Compounds.**—In nearly every case the reaction depends on the elimination of the two nitrogen atoms as nitrogen gas.

(1) When boiled with water a **phenol** is formed. The best yields are obtained when the diazo sulphate is used instead of the chloride :

$$C_6H_5N_2.HSO_4 + H.OH = C_6H_5OH + N_2 + H_2SO_4$$

(2) When boiled with strong hydrochloric acid an **aryl chloride** is produced. The yield is poor. Halides are usually prepared by methods (6) or (7) :

$$C_6H_5N_2Cl = C_6H_5Cl + N_2$$

(3) When boiled with alcohol (in which case the whole diazotisation must have taken place in alcohol, using amyl nitrite or sulphuric acid and solid sodium nitrite) a **hydrocarbon** is produced and the alcohol is oxidised to aldehyde :

$$C_6H_5N_2Cl + C_2H_5OH = C_6H_6 + N_2 + HCl + C_2H_4O$$

At the same time another reaction takes place, **an ether** being formed :

$$C_6H_5.N_2Cl + H.OC_2H_5 = C_6H_5OC_2H_5 + HCl + N_2$$

Phenyl ethyl ether, phenetole

(4) When treated with a solution of bromine in potassium bromide, a red oil, **diazobenzene perbromide**, $C_6H_5N_2Br_3$, is precipitated :

$$C_6H_5N_2Cl + KBr = C_6H_5N_2Br + KCl$$
$$C_6H_5N_2Br + Br_2 = C_6H_5N_2Br_3$$

(5) When added to potassium iodide solution the diazo iodide produced immediately decomposes, yielding an aryl iodide. This is the only method for making aryl iodides :

$$C_6H_5N_2I = C_6H_5I + N_2$$

(6) **Sandmeyer's Reaction.**—When a diazo solution is added to a hot solution of cuprous chloride in hydrochloric acid a good yield of **aryl chloride** is obtained. The cuprous salt exerts a catalytic action :

$$C_6H_5N_2Cl = C_6H_5Cl + N_2$$

If cuprous bromide (made from copper sulphate, copper, hydrochloric acid and potassium bromide) is used, **bromobenzene** is produced :

$$2\ C_6H_5N_2Cl + Cu_2Br_2 = 2\ C_6H_5Br + 2\ N_2 + Cu_2Cl_2$$

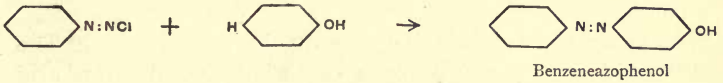
If a solution of cuprous cyanide in potassium cyanide (made by adding excess of potassium cyanide to copper sulphate solution) is used, a **nitrile** is obtained and from this a carboxylic acid may be prepared by hydrolysis:

$$2\,C_6H_5N_2Cl + Cu_2(CN)_2 = 2\,C_6H_5CN + Cu_2Cl_2 + N_2$$

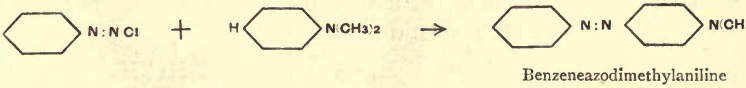
In each case the reaction product is steam distilled off and separated from the distillate. Good yields are obtained, and this method is almost invariably used for preparing these three types of compounds.

(7) **Gattermann's reaction** is similar to the Sandmeyer reaction but the hot cuprous solution is replaced by cold, finely-divided copper made by the action of zinc dust on copper sulphate. The yields are somewhat better than with the Sandmeyer reaction.

(8) When added to a solution of a phenol in caustic soda or to many amines in acetic acid solution highly coloured **azo dyes** are formed:




Benzeneazophenol




Benzeneazodimethylaniline

When treated with a hydrochloric acid solution of stannous chloride reduction takes place and **phenylhydrazine** is produced.

The diazo solution is prepared, using the smallest possible quantities of water, and is added to an ice-cold saturated solution of stannous chloride in strong hydrochloric acid, when the mixture solidifies to a mass of white crystals of phenylhydrazine hydrochloride:

$$C_6H_5N:NCl + 4\,H = C_6H_5NH.NH_2.HCl$$

The free base is prepared by filtering, adding excess of caustic soda, extracting with ether and fractionating *in vacuo*.

**Phenylhydrazine**, $C_6H_5NH.NH_2$, is a colourless solid melting at 20° and boiling at 240° with slight decomposition.

It readily turns brown on keeping and the impurities thus formed depress the melting-point below the ordinary temperature. Phenyl hydrazine is strongly basic and possesses a characteristic odour. It is extremely poisonous and is insoluble in water but dissolves readily in acids and yields crystalline salts. The hydrochloride is sparingly soluble in dilute hydrochloric acid. Like hydrazine it is a powerful reducing agent, reducing Fehling's solution in the cold :

$$C_6H_5NH \cdot NH_2 + 2\,CuO = C_6H_6 + N_2 + Cu_2O + H_2O$$

On reduction with zinc dust and acid it yields aniline and ammonia :

$$C_6H_5NH \cdot NH_2 + 2\,H = C_6H_5NH_2 + NH_3$$

It is extensively used as a test for aldehydes, ketones and sugars as the phenylhydrazones and osazones are as a rule well-defined crystalline solids of definite melting-point. It is also used in the synthesis of certain heterocyclic compounds, such as antipyrin.

(10) When diazobenzene chloride is treated with aniline a yellow solid is precipitated, especially if sodium acetate is added to remove mineral acid which prevents the condensation. The same result is obtained if excess of aniline or a deficit of acid are employed in the diazotisation of aniline. The substance is formed according to the equation :

$$C_6H_5N : N\overset{\cdots\cdots}{Cl} + H\overset{\cdots\cdots}{N}HC_6H_5 = C_6H_5N : N \cdot NHC_6H_5$$

and is known as diazoaminobenzene.

**Diazoaminobenzene,** $C_6H_5N_2 \cdot NHC_6H_5$, crystallises from alcohol in yellow prisms, melting at 92° and decomposing when kept at this temperature for any considerable time. It is decomposed by strong hydrochloric acid into its generators, diazobenze chloride and aniline. It is of importance on account of the molecular rearrangement it undergoes when warmed in aniline solution with a trace of aniline hydrochloride. The rearrangement resembles the benzidine transformation :

Diazoaminobenzene Aminoazobenzene

The product is **aminoazobenzene**, which may also be prepared by reducing nitroazobenzene.

The preparation is carried out by dissolving the diazoaminobenzene in aniline, adding a few grams of aniline hydrochloride and keeping the solution at 30° for a day. On acidifying with slightly diluted hydrochloric acid, blue crystals of aminoazobenzene hydrochloride are deposited and these on treatment with alkali yield the free base, which may be purified by crystallisation from alcohol.

**Aminoazobenzene**, $C_6H_5N_2C_6H_4NH_2$, forms yellow needles melting at 124°. It gives yellow solutions, which turn red on treatment with acids, owing to salt formation. The hydrochloride forms blue crystals, which dissolve to a red solution, which dyes cloth yellow. It was at one time employed as the dyestuff **aniline yellow**. Like all azo compounds it is reduced by stannous chloride, the azo double bond being broken and a mixture of aniline and phenylenediamine hydrochlorides being formed:

$$C_6H_5N=N.C_6H_4NH_2+4H=C_6H_5NH_2+NH_2C_6H_4NH_2$$

Aminoazobenzene is one of the simplest of the azo dyestuffs, which are dealt with more fully in the succeeding chapter.

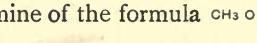
### Constitution of the Diazo Compounds

The constitution of these compounds (taking diazobenzene chloride as a type) has so far been assumed to be $C_6H_5.N:N.Cl$. This explains quite satisfactorily the formation of phenylhydrazine and of diazoaminobenzene. On the other hand these salts display a great similarity to the ammonium salts. Thus they are white crystalline solids soluble in water and are highly ionised in solution. The salts with strong acids are neutral but the hydroxide and carbonate (obtained from the chloride by means of silver hydroxide or carbonate) are strongly alkaline. The radical $C_6H_5N_2$ resembles the radical **ammonium**, $NH_4$, and is therefore usually termed **diazonium**, diazotised aniline hydrochloride therefore being called **benzene diazonium chloride**. Following this analogy we must assume that the nitrogen atom

attached to chlorine is pentavalent since no salts of nitrogen compounds are known without the basic nitrogen atom being pentavalent (cf. $NH_4Cl$, $N(CH_3)_4I$).

Benzene diazonium chloride then possesses the formula $C_6H_5—N—Cl$, and in solution exists as the ions

$$C_6H_5—N\equiv N \qquad \left[C_6H_5—N\equiv N\right]^{\cdot} \text{ and } Cl'$$

This theory has been confirmed by Hantzsch, who has prepared from *p*-anisidine (an amine of the formula  ) three isomeric diazo cyanides of the formula $RN_2CN$ (where $R = CH_3O.C_6H_4—$).

One of these is strongly ionised in solution and therefore contains pentavalent nitrogen, *i.e.* is the **diazonium cyanide**, $R—N\equiv N.CN$

The other two are unionised (therefore only containing trivalent nitrogen) and must be formulated $R—N{=}N—CN$ and $R—N{=}N—CN$ an isomerism parallel with the fumaric-maleic acid isomerism:

| | |
|---|---|
| HC . COOH | H . C . COOH |
| ‖ | ‖ |
| HC . COOH | HOOC . CH |
| Maleic acid | Fumaric acid |

These compounds may be called **diazocyanides**. One of them loses nitrogen very readily, yielding a nitrile, while the other is more stable. The former is known as the **syn-diazocyanide** and probably has the constitution $R—N{=}N—CN$ where R and CN are adjacent, while the more stable compound is the **anti-diazocyanide** and has the formula $R—N{=}N—CN$

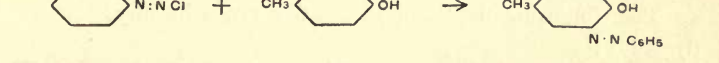
## CHAPTER X

### THE AZO DYESTUFFS

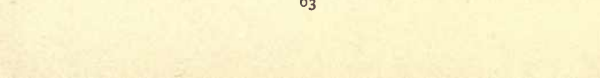
THE parent member of this series, azobenzene, has already been described (p. 36). When the hydrogen atoms of the benzene nuclei are replaced by amino or hydroxyl groups, the important technical products known as the *azo dyestuffs* are obtained.

**Preparation.**—These substances are prepared by "*coupling*" a diazo solution with a phenol or amine. In the first case the diazo solution is poured into a solution of the phenol in excess of dilute caustic soda, and after standing for some time the solution is neutralised when the azo colour is precipitated. In coupling with an amine the latter is dissolved in dilute acetic acid and the diazo solution added to this. Sodium acetate is then added to remove the mineral acid liberated in the reaction, since this tends to prevent coupling.

**Position of Coupling.**—Whenever possible, coupling takes place in the *para* position to the $NH_2$ or OH group. Thus:




When the *para* position is occupied coupling takes place **ortho** to these groups. Thus:

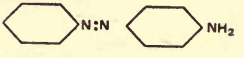



If both ortho and para positions are substituted no reaction takes place. Coupling **never** takes place in the *meta* position to the OH or $NH_2$ group.

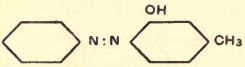
### Nomenclature

This may most readily be gathered from the following examples:

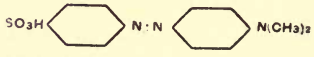
Benzeneazophenol, hydroxyazobenzene



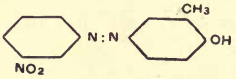

Benzeneazoaniline, aminoazobenzene




Benzeneazo-*m*-cresol




*p*-Sulphobenzeneazodimethylaniline




*m*-Nitrobenzeneazo-*o*-cresol

*p*-Nitrobenzeneazo-*o*-toluidine

**Colour.**—No definite rules can be laid down, but the following generally hold good:

(1) Azo colours are usually yellow, red or brown.

(2) The simplest azo compounds are yellow or light red. As the molecular complexity of the components increases the colour deepens, giving blues, violets, and blacks. These latter are usually obtained from naphthylamines and naphthols.

(3) The dyestuffs produced by coupling with hydroxycarboxylic acids (such as salicylic acid) are light yellow.

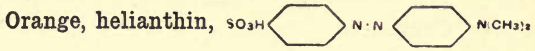
**Sulphonation** is frequently resorted to in order to increase the solubility of the colouring matter (which otherwise is insoluble in water). This may be accomplished either by sulphonating the finished product or, more usually, by using already sulphonated components (such as sulphanilic acid and naphthol sulphonic acids).

The following list comprises a few types of important azo dyestuffs:

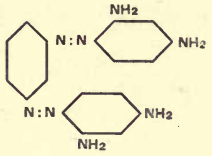
(1) **Aniline Yellow** (p. 61)

, Aminoazobenzene. Prepared by molecular rearrangement of diazoamino-

benzene. The hydrochloride (usually of the sulphonated compound) was formerly sold as "aniline yellow."

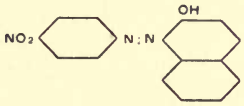
(2) **Methyl Orange, helianthin,** 


*p*-sulphobenzeneazodimethylaniline. Prepared by coupling diazotised sulphanilic acid with dimethylaniline. Used as an indicator.

(3) **Bismarck Brown,** 

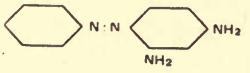
, by treating *m*-phenylenediamine with nitrous acid.

One molecule is completely diazotised and each diazo group couples with a fresh molecule of the diamine.

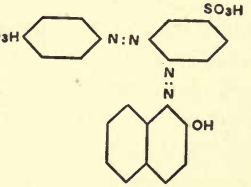
(4) ***p*-Nitraniline Red,** 

, *p*-nitrobenzeneazo *β*-naphthol.

The most important of the red azo dyes. Prepared from diazotised *p*-nitraniline and *β*-naphthol.

(5) **Chrysoïdine,** 

, benzeneazo *m*-phenylenediamine. Prepared by coupling diazotised aniline with *m*-phenylenediamine.

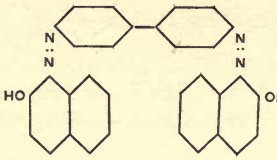
(6) **Biebrich Scarlet,** 

, *p*-sulphobenzeneazo *p*-sulphobenzeneazo *β*-naphthol.

This type of compound is known as a **tetrazo dye,** since it has two azo groups.

Sulphanilic acid is diazotised and coupled with itself and the resulting amino compound is then diazotised and coupled with β-naphthol.

(7) **Congo Red,**




This is a typical benzidine dyestuff prepared from "tetrazotised" benzidine and β-naphthol. From various sulphonic acids of α- and β-naphthols a range of "Congo" colours are prepared.

**Mordants.**—It will be noticed that all the above-mentioned dyestuffs are amines or phenols, *i.e.* are able to form salts with acids and bases respectively. If an animal fibre such as silk or wool is treated with a solution of one of these dyestuffs the colour it acquires is "fast" and cannot be removed by extracting the fibre with solvents in which the dyestuff is soluble. If, on the other hand, a vegetable fibre such as cotton is treated with the dyestuff the colour is not "fast" unless there is also present some substance which will form an insoluble salt with the dyestuff. One of the most important mordants is aluminium hydroxide. This has the advantage of being an "amphoteric" compound, *i.e.* one which can react either as an acid or as a base. When a vegetable fibre impregnated with aluminium hydroxide is placed in a bath containing an azophenol, the insoluble aluminium salt of this phenol is precipitated in the fibre. In the case of an aminoazo compound the insoluble salt is the aluminate of the base. The animal fibres which do not require mordanting have been shown to contain amphoteric organic compounds which react in the same way as the artificially applied mordant.

The azo dyes from benzidine are of great technical value since they are "*substantive*," *i.e.* will dye unmordanted cotton.

## CHAPTER XI

### THE PHENOLS

THE hydroxy derivatives of the aromatic hydrocarbons may be divided into two classes:

(1) Those in which the hydroxyl group replaces a hydrogen atom of the benzene nucleus. These substances are known as **phenols.**

(2) Those in which the hydroxyl group replaces a hydrogen atom in a side chain. These are known as the **aromatic alcohols.**

These two classes are entirely different in chemical properties, the latter resembling the aliphatic alcohols in their reactions while the former, which will be dealt with in this chapter, have no aliphatic analogues.

The phenols again may be classified as monohydric, dihydric, trihydric, etc., according to the number of hydroxyl groups they contain.

**Preparation.**—There are two general methods for the preparation of phenols:

(*a*) Fusion of a sulphonic acid with caustic potash:

$$C_6H_5SO_3K + KOH = C_6H_5OH + K_2SO_3$$

The melt which contains the phenol as its potassium salt is extracted with water and acidified and the phenol extracted by suitable means.

This reaction is usually employed in technical practice:

(*b*) Boiling a diazo salt (preferably the sulphate) with water:

$$C_6H_5N_2HSO_4 + H_2O = C_6H_5OH + N_2 + H_2SO_4$$

This method is generally used in the laboratory.

There are several other methods which are employed in

particular cases, notably the distillation of hydroxy acids with or sometimes without lime:

$$C_6H_4(OH).COOH + CaO = C_6H_5OH + CaCO_3$$

**Properties.**—The phenols are colourless solids of low melting-point and possessing a sweet and burning taste. They are powerful antiseptics. The monohydric phenols are sparingly soluble in water and are usually volatile in steam. As the number of hydroxyl groups increases the solubility in water rapidly increases and the volatility in steam diminishes. All phenols are readily **soluble in caustic alkalis** and yield crystalline salts on concentration of the solutions. Unless other acid groups such as $NO_2$ or halogen are present the phenols are not sufficiently strong acids to decompose carbonates and may therefore be liberated from their salts by carbon dioxide. The alkaline solutions absorb oxygen from the air, becoming dark brown, complete disruption of the benzene ring taking place. The action is slow in the case of monohydric phenols but is very rapid with trihydric phenols such as pyrogallol.

Nearly all phenols give **colour reactions with ferric chloride,** monohydric and metadihydric phenols giving purple and dihydric phenols green colorations. They also give the **Liebermann test.** This is carried out by dissolving a trace of any nitroso compound (or sodium nitrite) in strong sulphuric acid, adding a crystal of the phenol and warming. A green solution is obtained which becomes red on diluting with water and blue on making alkaline. This reaction also serves as a test for a nitroso compound. Since phenols contain the (OH) group they give the usual reactions with sodium, phosphorus pentachloride, acetic anhydride, etc. The majority when dissolved in alkali couple with diazo salts, forming azo dyestuffs.

When the alkali salts are heated with alkyl halides the corresponding ethers are formed:

$$C_6H_5ONa + CH_3I = C_6H_5OCH_3 + NaI$$

### Monohydric Phenols

**Phenol,** carbolic acid, $C_6H_5OH$. This substance is obtained

from the middle or carbolic oil (b.p. 170–230°) from coal tar in the following way:

The oil is allowed to stand for some weeks in a cold place, when the bulk of the naphthalene crystallises out and is removed. The liquid is then agitated with dilute caustic soda and the solution separated from any oily hydrocarbons and boiled. It is then strained from tarry matter and acidified, when crude phenol mixed with its homologues separates as an oil. This is separated, purified by careful fractional distillation, and for medical purposes finally purified by distillation with litharge, which retains traces of sulphur compounds.

As thus prepared phenol is a white crystalline solid melting at 42° and boiling at 184°. It possesses a sweet, burning taste and characteristic odour, is an excellent antiseptic and blisters the skin. When mixed with a small amount of water it melts and yields a homogeneous liquid which, on further addition of water, at first separates into two layers and finally the phenol completely dissolves. The solution gives a purple colour with ferric chloride, and even when very dilute gives with bromine water a quantitative precipitate of white insoluble **tribromophenol** (2.4.6.). Phenol, being a hydroxy compound, yields an acetate when boiled with acetic anhydride. Phenyl acetate is a colourless liquid boiling at 195°. Phenyl benzoate (or benzoyl phenol) is best prepared by the **Shotten-Baumann reaction,** a method which is almost universally employed for benzoylating hydroxy compounds. The phenol is dissolved in excess of dilute caustic soda in a flask and slightly more than the theoretical amount of benzoyl chloride is added. The flask is then corked and shaken vigorously until the odour of benzoyl chloride has disappeared. The precipitated benzoyl compound is then filtered off and recrystallised.

**Phenyl Ethers.**—These are prepared by adding one molecular proportion of phenol to a solution of one molecular proportion of sodium in a suitable alcohol. To the solution of sodium phenate thus formed the theoretical quantity of alkyl iodide is added, the whole refluxed for an hour and the ether

isolated by pouring into water, extracting with ether, drying and fractionating:

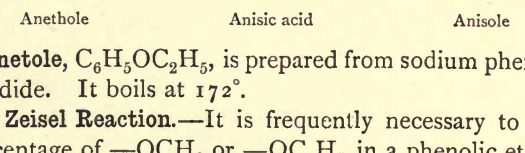
$$C_6H_5OH + CH_3ONa = C_6H_5ONa + CH_3OH$$
$$C_6H_5ONa + CH_3I = C_6H_5OCH_3 + NaI$$

The ethers are liquids with an aromatic odour, insoluble in water and very stable towards reagents. They are decomposed by heating with hydriodic acid:

$$C_6H_5OCH_3 + HI = C_6H_5OH + CH_3I$$

**Anisole**, $C_6H_5OCH_3$, is prepared by the method described above. It boils at 155°. It was originally prepared by distilling anisic acid with lime.

Anisic acid is prepared by the oxidation of anethole (the chief constituent of oil of aniseed) by means of potassium permanganate:




Anethole — Anisic acid — Anisole

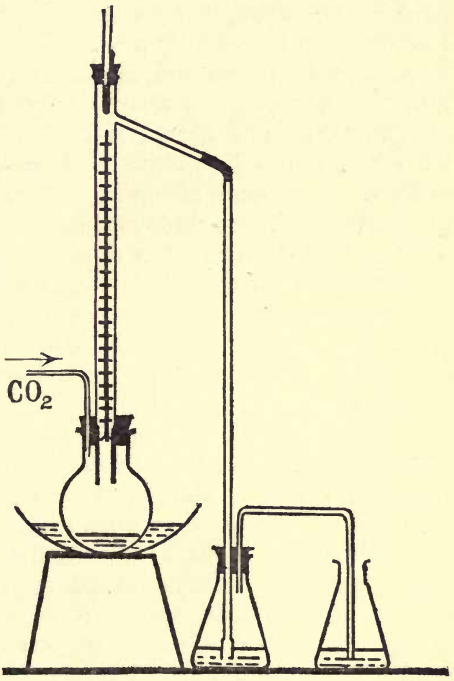
**Phenetole**, $C_6H_5OC_2H_5$, is prepared from sodium phenate and ethyl iodide. It boils at 172°.

**The Zeisel Reaction.**—It is frequently necessary to estimate the percentage of $-OCH_3$ or $-OC_2H_5$ in a phenolic ether, particularly in investigations on the constitution of alkaloids, which usually contain several of these groups. The method consists in heating the ether with **concentrated hydriodic acid** and conducting the evolved vapours into an aqueous-alcoholic solution of silver nitrate, when the following reactions take place:

$$ROCH_3 + HI = ROH + CH_3I$$
$$CH_3I + H_2O + AgNO_3 = AgI + CH_3OH + HNO_3$$

A weighed amount of the ether is mixed with concentrated hydriodic acid in a bulb fitted with a rod and disc column (to act as a reflux condenser for the hydriodic acid) and heated to 140°

in an oil bath for two hours. A slow current of carbon dioxide is passed through the apparatus and into two flasks containing the silver nitrate. The volatile alkyl iodide is carried over with the carbon dioxide and precipitates the equivalent amount of silver iodide, which is finally weighed. Every 235 grms. of silver iodide are thus equivalent to 31 grms. of $-OCH_3$ (methoxyl) or 45 grms. of $-OC_2H_5$ (ethoxyl).




**Halogen Compounds**

The mono-halogen compounds of phenol are prepared by the direct action of the halogen on pure phenol. A mixture of *ortho* and *para* derivatives is obtained. They may also be prepared by diazotising the corresponding chlor- or brom-anilines and boiling the product with water.

The halogen-substituted phenols resemble phenol very closely but are more strongly acid and will decompose sodium carbonate.

*o*-**Chlorophenol** is a liquid boiling at 176°.

*m*-**Chlorophenol** boils at 212°. It is prepared from *m*-chloraniline (p. 46) by the diazo reaction.

*p*-**Chlorophenol** is a solid melting at 41° and boiling at 217°.

*Sym.* **Tribromophenol** is a white insoluble solid produced when phenol is treated with bromine water. It melts at 92°.

### Nitro Compounds

The presence of the hydroxyl group in the benzene ring renders the latter more susceptible to substitution. Thus bromine water immediately produces a tribromo derivative, and mono-nitro derivatives can be obtained by the action of dilute nitric acid without the presence of sulphuric acid.

The nitration of phenol is carried out by adding melted phenol to cold dilute nitric acid and cooling the reaction mixture. A mixture of ortho and para nitro-compounds is produced, the former predominating if the acid becomes at all warm. After standing for a short time the heavy black oil is separated from any unused nitric acid and steam distilled, when the ortho compound alone passes over. The para compound is isolated from the tarry residue by extraction with boiling water containing animal charcoal and crystallisation from hot water.

The nitrophenols are sufficiently acid to decompose sodium carbonate, the solutions of the sodium salts being a deep yellow. The nitrophenols give **no coloration with ferric chloride** nor do they readily couple with diazo salts. The nitrophenols and their salts decompose with a slight explosion on heating.

*o*-**Nitrophenol** forms yellow needles melting at 45°. It is slightly soluble in water, volatile in steam, and possesses a characteristic phenolic odour. It dissolves readily in alkalis, giving an intense yellow solution; and on concentration of its caustic soda solution magnificent crimson needles of **sodium** *o*-**nitrophenate** are deposited.

*p*-**Nitrophenol**, which is formed at the same time as the ortho isomeride but is not volatile in steam, forms long white odourless needles soluble in hot water and melting at 114°. The sodium salt is bright yellow both in solution and in the solid state. It is sometimes used as an indicator.

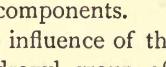
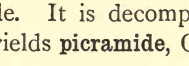
*Sym.* **Trinitrophenol, Picric Acid,** is the ultimate nitration product of phenol. It is prepared by dissolving phenol in strong sulphuric acid, adding this solution to a mixture of ordinary strong and fuming nitric acid and heating the mixture for several hours on the water-bath. On pouring into water the picric acid

is precipitated and is purified by recrystallisation from boiling water. If no fuming nitric acid is used or if the heating is not sufficient, the picric acid will be mixed with a considerable amount of 2.4 dinitrophenol. Picric acid is also formed when 1.3.5 trinitrobenzene is treated with potassium ferricyanide. It is frequently formed by the action of nitric acid on organic compounds. The yellow stain produced by the action of nitric acid on the skin is due to the formation of picric acid, and this substance was first prepared by the nitration of silk. It was formerly used as a yellow dyestuff for silk and wool.

Picric acid crystallises in yellow plates sparingly soluble in cold water and possessing an intensely bitter taste. It melts at 122° and decomposes with a slight explosion at higher temperatures. When it is detonated in a closed space it explodes violently, its salts possessing the same property. It forms the basis of the explosive *lyddite*.

Picric acid is of considerable use in the laboratory owing to its power of forming well-defined crystalline addition compounds of definite melting-point with many aromatic substances, notably naphthalene, anthracene and the alkaloids. These "**picrates**" are usually prepared by mixing aqueous, alcoholic or benzene solutions of the components.

Owing to the influence of the three acid nitro groups on the already acid hydroxyl group of phenol, picric acid behaves in all respects as a *strong acid*. On treatment with phosphorus pentachloride it yields **picryl chloride**, $C_6H_2(NO_3)Cl$, which reacts as a typical acid chloride. It is decomposed by water, fumes in air and with ammonia yields **picramide**, $C_6H_2(NO_2)_3NH_2$.

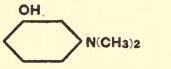
*p*-**Nitrosophenol**,  is precipitated when an ice-cold aqueous solution of phenol is treated with nitrous acid. It is also formed when *p*-nitrosodimethylaniline is boiled with caustic soda. It forms dark greenish-brown plates. It is identical with the quinone oxime,  produced when quinone is

treated with hydroxylamine. It thus affords an example of **tautomerism** (cf. Ethyl acetoacetate and phloroglucinol).

**Amino Phenols.**—These substances are prepared by the reduction of nitrophenols, usually by ammonium sulphide. The para compound is also prepared by the reduction of benzeneazophenol by means of stannous chloride and hydrochloric acid:

$$C_6H_5N:N.C_6H_4OH + 4H = C_6H_5NH_2 + NH_2C_6H_4OH$$

The aminophenols are white crystalline solids which, like the diamines, oxidise and darken very rapidly in air, particularly when in alkaline solution. For this reason some derivatives are used in photography as developers for reducing the exposed image to metallic silver. Thus *rhodinal* is *p*-aminophenol and *metol* is *m*-amino-*p*-cresol (1 oxy- 3 amino- 4 methylbenzene). They combine the reactions of amines and phenols, being soluble both in acids and alkalis, diazotising and also coupling with diazo compounds.

**Dimethyl *m*-aminophenol,** 

is prepared by sulphonating dimethylaniline (an exception to Crum Brown and Gibson's Rule) and fusing the product with potash. It is used in the preparation of the *rhodamine dyestuffs* (p. 98).

***p*-Aminophenol** is prepared from *p*-nitrophenol and from benzeneazophenol. On oxidation with chromic acid mixture it yields **quinone** (p. 85).

***p*-Aminophenetole,** *p*-phenetidine, $C_2H_5O.C_6H_4.NH_2$, is prepared by boiling *p*-nitrophenol with sodium carbonate and ethyl iodide and reducing the resulting *p*-nitrophenetole. It is a colourless, odourless basic liquid boiling at 245°.

**Phenacetin,** $C_2H_5O.C_6H_4.NH.COCH_3$, is the acetyl derivative of *p*-phenetidine and is a most important drug. It is a white crystalline solid melting at 135°.

**Cresols.**—These substances are the mono-hydroxy derivatives of toluene. They occur with phenol in the *middle oil* and form the higher boiling fraction of the crude phenol. As a rule they are not separated but are used as a substitute for phenol in

the preparation of disinfectants. They possess very similar properties to phenol, but have a rather more unpleasant odour and a higher boiling-point.

The pure compounds are best prepared by the diazo reaction from the corresponding toluidines. The ortho and para compounds are solids melting at 30° and 36°, while *m*-cresol is a liquid.

### Dihydric Phenols

These differ from the monohydric phenols in being more soluble in water, more easily oxidised in alkaline solution (and therefore more powerful reducing agents), and possessing higher melting-points.

**Catechol**, *o*-dioxybenzene, is formed when certain resins are fused with potash and when phenol *o*-sulphonic acid is similarly treated. It is prepared by heating **guaiacol**, its monomethyl ether with hydriodic acid (the Zeisel reaction).

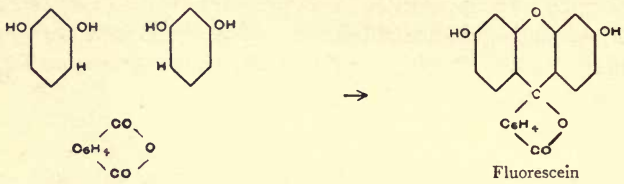
Catechol forms colourless crystals melting at 105°. It gives a green coloration with ferric chloride and reduces Fehling's solution.

**Guaiacol**, $o\text{-}C_6H_4(OH)OCH_3$, is present in beech-wood tar, from which it can be isolated in the same way as phenol is from coal tar. It forms large transparent crystals melting at 28° and possessing a characteristic unpleasant odour. It reacts both as a phenol and an ether. It gives a green coloration with alcoholic ferric chloride.

**Resorcinol**, *m*-dioxybenzene, the most important of the dihydric phenols, is prepared by fusing benzene *m*-disulphonic acid with potash. It is also formed when *o*- and *p*-chlorophenols are fused with alkali at a high temperature.

Resorcinol forms colourless needles melting at 119° and possessing a sweet taste. It is very soluble in water and the solution reduces ammoniacal silver nitrate and Fehling's solution. It also yields a purple coloration with ferric chloride and a white precipitate of a tribromo-derivative with bromine water. Resorcinol is used technically for the preparation of **fluorescein** (p. 98), and may be readily identified by this reaction. When

resorcinol is fused with phthalic anhydride and a drop of strong sulphuric acid fluorescein is formed, which dissolves in caustic soda with a magnificent yellow-green fluorescence (cf. p. 98):



Fluorescein

**Quinol**, hydroquinone, *p*-dioxybenzene, occurs naturally in the glucoside arbutin. It is usually prepared from quinone (p. 85) by reduction with sulphur dioxide. It forms colourless needles (m.p. 169°) which are very soluble in water and in alkaline solution it forms a powerful reducing agent (hence its use as a developer). With oxidising agents, such as ferric chloride or potassium dichromate, yellow quinone is produced and may be identified by its pungent odour.

### Trihydric Phenols

Only two of these (the 1.2.3 and the 1.3.5) are of importance.

**Pyrogallol**, pyrogallic acid, 1.2.3 trioxybenzene, is prepared by distilling **gallic acid**, which occurs in oak galls.

Gallic acid Pyrogallol

It forms colourless needles melting at 132°. It is very soluble in water and the solution when alkaline absorbs oxygen very rapidly, and is therefore used for this purpose in gas analysis. It is the most important of the photographic developers.

Pyrogallol gives a red colour with ferric chloride and a blue coloration with ferrous sulphate.

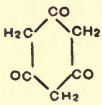
**Phloroglucinol** *sym.* trioxybenzene, is a constituent of

many resins and in combination as the glucoside phloridzin exists in the bark of fruit trees. It is best prepared by fusing resorcinol with potash, oxidation taking place:

$$C_6H_4(OH)_2 + O = C_6H_3(OH)_3$$

It is also formed by condensation of three molecules of sodiomalonic ester (p. 12).

Phloroglucinol is a colourless solid very soluble in water and melting at 218°. The solution reduces Fehling's solution and gives a purple colour with ferric chloride. Like other polyhydric phenols the alkaline solution turns brown in air.

Though phloroglucinol behaves as a trihydroxy compound, yielding a **triacetate** with acetic anhydride, it also reacts as if it possessed the formula  , yielding a **trioxime** with hydroxylamine.

Here (as with ethylacetoacetate, nitrosophenol, etc.) we have an example of a tautomeric substance.

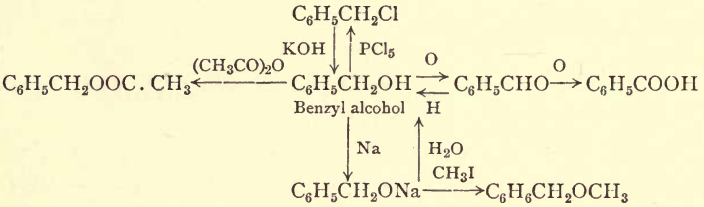
**Hexahydroxybenzene,** $C_6(OH)_6$. The potassium salt of this phenol is produced when carbon monoxide is passed over heated potassium.

## CHAPTER XII

## ALCOHOLS, ALDEHYDES, KETONES AND QUINONES

### Alcohols

THE aromatic alcohols are produced by the replacement of side-chain hydrogen atoms by hydroxyl. They strongly resemble their aliphatic analogues in their reactions. Thus :




**Benzyl alcohol,** $C_6H_5CH_2OH$, may be prepared by boiling benzyl chloride with sodium carbonate or hydroxide or by reducing benzaldehyde with sodium amalgam. It is usually prepared by the **Cannizzaro reaction,** which is peculiar to the aromatic aldehydes. (There is one exception to this statement, formaldehyde reacting in the same way with alkalis.)

This reaction consists in allowing benzaldehyde to stand for some hours with a saturated solution of caustic potash, when two molecules of the former undergo mutual oxidation and reduction :

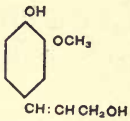
$$2\,C_6H_5CHO + H_2O = C_6H_5CH_2OH + C_6H_5COOH$$

The benzyl alcohol is isolated by dilution and extraction with ether.

Benzyl alcohol is a colourless liquid with a faint aromatic odour, partially miscible with water and boiling at 204°. It possesses all the usual properties of a primary alcohol. On

oxidation it yields first benzaldehyde and finally benzoic acid. **Benzyl acetate** is a colourless liquid boiling at 206° and possessing a fragrant odour. It is a constituent of oil of jasmine.

**Saligenin,** salicyl alcohol, $o\text{-}C_6H_4\begin{cases}CH_2OH\\OH\end{cases}$ occurs as a glucoside, **salicin,** in the bark of the willow. It is prepared by the reduction of salicyl aldehyde by sodium amalgam.

**Coniferyl alcohol,**  is obtained by the hydrolysis of **coniferin,** a glucoside obtained from the *Coniferæ*. On oxidation it is converted into **vanillin** (p. 83):

Coniferyl alcohol — Vanillin

**Benzhydrol,** $(C_6H_5)_2CHOH$, is prepared by the reduction of benzophenone, $(C_6H_5)_2CO$, by sodium amalgam, or, better, by the **Grignard reaction** (p. 132) from benzaldehyde and magnesium phenyl bromide:

$$C_6H_5CHO + MgC_6H_5Br \longrightarrow C_6H_5CH\begin{cases}O\cdot MgBr\\C_6H_5\end{cases}HO\cdot H \longrightarrow (C_6H_5)_2CHOH + MgBr(OH)$$

It is a crystalline solid melting at 68°.

**Triphenylcarbinol,** $(C_6H_5)_3COH$, may be prepared by oxidising triphenylmethane (p. 100) with chromic acid or from benzophenone and magnesium phenyl bromide. It is a white solid melting at 160° and is the parent of the magenta dyestuffs.

## Aldehydes

The aromatic aldehydes resemble those of the aliphatic series in most respects but differ from them in undergoing the Cannizzaro and Perkin reactions (pp. 78 and 90).

They possess pleasant odours and a large number are used as flavouring essences.

**Benzaldehyde,** $C_6H_5CHO$, occurs as the glucoside **amygdalin** in oil of bitter almonds. This glucoside is hydrolysed by the accompanying **enzyme emulsin** to hydrocyanic acid, benzaldehyde and glucose. It is also formed by the following methods:

(1) Oxidation of benzyl alcohol with chromic acid mixture.

(2) Distillation of calcium benzoate with calcium formate:

$$(C_6H_5COO)_2Ca + (HCOO)_2Ca = 2\ CaCO_3 + 2\ C_6H_5CHO$$

(3) Hydrolysis of benzal chloride by heating with milk of lime under pressure:

$$C_6H_5CHCl_2 + CaO = C_6H_5CHO + CaCl_2$$

(4) Hydrolysis and oxidation of benzyl chloride by boiling with a solution of copper nitrate:

$$C_6H_5CH_2Cl + HOH = C_6H_5CH_2OH + HCl$$
$$C_6H_5CH_2OH + O = C_6H_5CHO + H_2O$$

(5) Oxidation of toluene by digestion with manganese dioxide and sulphuric acid.

(6) Oxidation of toluene by the **Etard reaction.** This consists in carefully mixing toluene with chromyl chloride and pouring the explosive solid addition compound into water.

In each case the benzaldehyde is isolated by steam distillation and ether extraction, these operations being carried out in a current of carbon dioxide since benzaldehyde readily oxidises on free exposure to air.

Of the above methods (1) and (2) are only of theoretical interest.

Methods (3) and (4) are technically important, particularly the former, by which nearly all benzaldehyde is prepared.

Methods (5) and (6), particularly the latter, are sometimes employed in the laboratory for the preparation of certain substituted benzaldehydes from the corresponding substituted toluenes.

Benzaldehyde is a colourless liquid insoluble in water and boiling at 179°. It possesses a pleasant odour of bitter almonds

and is of considerable importance in the dye industry. On exposure to air it readily absorbs oxygen, forming crystals of benzoic acid.

It possesses many of the properties of aliphatic aldehydes, reducing ammoniacal silver solutions, forming a crystalline bisulphite compound, a cyanhydrin, an oxime and a phenylhydrazone, and with phosphorus pentachloride yielding benzal chloride. It does not reduce Fehling's solution.

The aromatic aldehydes, of which class benzaldehyde may be taken as typical, also undergo certain reactions which are without analogy among the aliphatic compounds.

(1) With concentrated alkali they undergo the **Cannizzaro reaction**:

$$2\,C_6H_5CHO + H_2O = C_6H_5CH_2OH + C_6H_5COOH$$

(2) On warming with primary amines benzylidine compounds are formed:

$$C_6H_5CH{:}O + H_2N \cdot C_6H_5 = C_6H_5CH : NC_6H_5$$

Benzylidine aniline

(3) On boiling with alcoholic potassium cyanide two molecules condense, forming **benzoin**:

$$2\,C_6H_5CHO = C_6H_5CHOH \cdot CO \cdot C_6H_5$$

Benzoin

(4) They condense with aliphatic aldehydes in the presence of dilute alkali, forming unsaturated aldehydes (the **Claisen reaction**):

$$C_6H_5CH{:}O + H_2CH \cdot CHO = C_6H_5CH : CH \cdot CHO$$

Cinnamic aldehyde

(5) On boiling with acetic anhydride (as dehydrating agent) and the sodium salt of a fatty acid they form an unsaturated acid (the **Perkin reaction**):

$$C_6H_5CH{:}O + H_2CH \cdot COONa \longrightarrow C_6H_5CH : CH \cdot COOH$$

Cinnamic acid

**Benzaldoximes.**—Benzaldoxime, prepared in the usual way from benzaldehyde, hydroxylamine hydrochloride and caustic soda, is a colourless crystalline solid melting at 34°.

If this oxime is dissolved in dry ether and saturated with hydrogen chloride a white hydrochloride is deposited which when

decomposed by sodium carbonate yields an isomeric benzaldoxime melting at 134° which is quite stable when pure.

This isomerism can be explained by assuming the two oximes to have structures similar to those of the *syn* and *anti* diazo compounds and maleic and fumaric acids, *i.e.*:

$$C_6H_5 . CH \quad \text{and} \quad C_6H_5 . CH$$
$$\quad\quad\| \qquad\qquad\qquad\quad \|$$
$$HON \qquad\qquad\qquad NOH$$

The first, where the hydrogen and hydroxyl groups are opposed, is known as **anti-benzaldoxime** and the second as **syn-benzaldoxime.** Since the isomer melting at 134° very readily loses water when warmed with dehydrating agents forming benzonitrile it is probably the *syn* oxime.

**Cinnamic aldehyde,** $C_6H_5 . CH : CH . CHO$, forms the chief constituent of oil of cinnamon and is used as a flavouring essence.

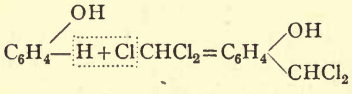
It is prepared by the *Claisen reaction* from benzaldehyde, acetaldehyde and dilute caustic soda:

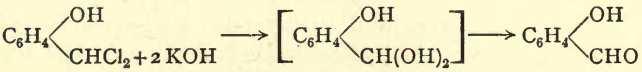
$$C_6H_5CHO + H_2CH . CHO = C_6H_5CH : CH . CHO + H_2O$$

It is a colourless oil with a fragrant odour and boils at 246°. It possesses all the properties of an aromatic aldehyde and also those of an unsaturated compound (forming a dibromide with bromine water). On oxidation it yields, firstly, cinnamic acid, and, finally, benzoic acid.

### Hydroxyaldehydes

**Salicylaldehyde,** *o*-hydroxybenzaldehyde, is the most important of these compounds. It is prepared by the **Reimer reaction** on boiling together under reflux phenol, caustic soda and chloroform:



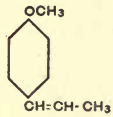


The salicylaldehyde is isolated by acidifying, distilling in steam and purifying by means of the bisulphite compound. At the same time a little *p*-oxybenzaldehyde is formed and remains behind, being non-volatile in steam.

Salicylaldehyde is a colourless liquid sparingly soluble in water, boiling at 196° and possessing a phenolic odour. It possesses the characteristic properties both of a phenol and of an aldehyde. It gives a purple colour with ferric chloride and is soluble in caustic soda, yielding a yellow solution.

***p*-Oxybenzaldehyde**, which is also formed in the Reimer reaction, is a white solid melting at 116°.

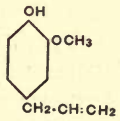
**Anisaldehyde**, *p*-methoxybenzaldehyde, is a colourless liquid boiling at 248° and possessing a pleasant odour. It may be prepared by methylating *p*-oxybenzaldehyde with sodium methoxide and methyl iodide or by carefully oxidising *anethole*, the chief constituent of aniseed oil, with dilute chromic acid.



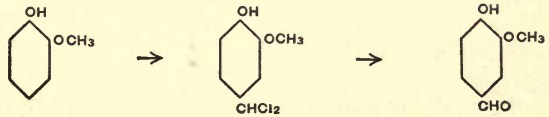
Anethole

Anisaldehyde

It may also be prepared by the Reimer reaction from anisol.

**Vanillin**, *m*-methoxy-*p*-oxybenzaldehyde, is the fragrant constituent of the *vanilla* bean. It forms colourless needles possessing an odour of vanilla, melting at 80° and readily subliming. It is prepared commercially by the careful oxidation of **eugenol** (oil of cloves), 

and also of coniferyl alcohol (p. 79). It may be synthesised by the Reimer reaction, using guaiacol, chloroform and caustic potash:



Guaiacol — Vanillin

## Ketones

These may be purely aromatic or mixed aromatic-aliphatic. They have the same general reactions as the aliphatic ketones.

**Acetophenone**, phenyl methyl ketone, $C_6H_5COCH_3$.

This is prepared by the Friedel and Crafts reaction, from benzene, acetyl chloride and anhydrous aluminium chloride:

$$C_6H_5{:}H + Cl{:}COCH_3 = C_6H_5COCH_3 + HCl$$

It is isolated by pouring the product into cold dilute acid and extracting the ketone with ether.

Acetophenone is also formed by the general method for the preparation of mixed ketones, *i.e.* by distillation of a mixture of calcium acetate and benzoate:

$$(C_6H_5COO)_2Ca + (CH_3COO)_2Ca = 2\,CaCO_3 + C_6H_5COCH_3$$

Acetophenone is a colourless crystalline solid melting at 21° and boiling at 207° and possessing a characteristic odour. It gives the usual reactions of a ketone with sodium amalgam, phenyl hydrazine, hydroxylamine and phosphorus pentachloride. On oxidation it yields benzoic acid.

**Benzophenone**, Diphenylketone, $(C_6H_5)_2CO$, may be prepared by the following reactions:

$$(C_6H_5COO)_2Ca \xrightarrow{\text{Distil}} (C_6H_5)_2CO + CaCO_3$$

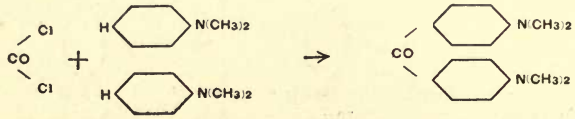
$$C_6H_5 . H + Cl . COC_6H_5 \xrightarrow{AlCl_3} C_6H_5COC_6H_5 + HCl \quad \textbf{(Friedel and Crafts)}$$

$$\underset{\text{Phosgene}}{C_6H_5H + ClCOCl + HC_6H_5} \xrightarrow{AlCl_3} (C_6H_5)_2CO + 2\,HCl \quad (\text{ ,, ,, })$$

It is a white crystalline solid with an unpleasant odour, melting at 48° and boiling at 305°.

**Michler's Ketone**, *p.p.*-tetramethyldiaminobenzophenone, is of considerable technical importance as it may be readily converted nto the dyestuffs auramine and methyl violet (pp. 102 and 104).

It is prepared from carbonyl chloride and dimethylaniline by the Friedel and Crafts reaction:




Michler's ketone

It is a white crystalline solid insoluble in water and melting at 172°.

**Benzoin,** $C_6H_5CHOH.CO.C_6H_5$, is prepared by boiling benzaldehyde with alcoholic potassium cyanide (p. 81):

$$2\,C_6H_5CHO = C_6H_5CHOH.COC_6H_5$$

It is a white crystalline solid melting at 137°. It reduces Fehling's solution, being oxidised to benzil.

**Benzil,** $C_6H_5CO.CO.C_6H_5$, is prepared by boiling benzoin with concentrated nitric acid:

$$C_6H_5CHOH.COC_6H_5 \xrightarrow{O} C_6H_5CO.CO.C_6H_5$$

It crystallises in yellow needles melting at 95°.

Benzil yields two isomeric monoximes and three dioximes:

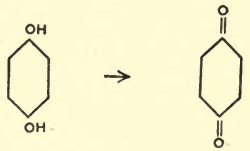
$$C_6H_5C(=HON).CO.C_6H_5 \qquad C_6H_5C(=NOH).CO.C_6H_5$$

$$C_6H_5C(=HON).C(=NOH).C_6H_5 \qquad C_6H_5C(=HON)-C(=HON).C_6H_5 \qquad C_6H_5.C(=NOH)-C(-HON).C_6H_5$$

## Quinones

These compounds have no analogues in the aliphatic series.

*p*-**Benzoquinone,** $C_6H_4O_2$, is formed when aniline, sulphanilic acid, *p*-aminophenol, *p*-phenylene diamine, or quinol are oxidised with chromic acid mixture. It is most simply prepared by warming quinol with ferric chloride:




Quinol Quinone.

It is usually prepared by allowing aniline to stand for some hours with potassium dichromate and sulphuric acid and extracting with ether. Benzoquinone as thus prepared forms

yellow prisms melting at 114° and is characterised by its acrid, irritating odour.

Quinone is readily reduced by sulphur dioxide to quinol, which is usually prepared by oxidising aniline, saturating with sulphur dioxide and extracting with ether.

Equimolecular proportions of quinone and quinol unite to form **quinhydrone**, a substance crystallising in greenish-black leaflets. This is frequently produced when quinol is oxidised with an insufficient amount of ferric chloride.

**Chloranil**, tetrachlorquinone, is produced if the above substances are oxidised with potassium chlorate and hydrochloric acid. It crystallises in yellow leaflets and is used commercially as an oxidising agent.

*o*-**Benzoquinone** is a red solid prepared by shaking an ethereal solution of catechol with dry silver oxide. It is unstable and may be readily reduced to catechol.

## CHAPTER XIII

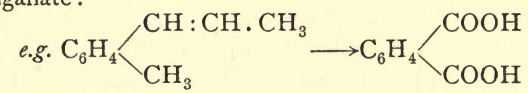
### AROMATIC ACIDS

THE acids of the aromatic series closely resemble the aliphatic acids in their chemical properties, the chief derivatives (esters, anhydrides, amides, etc.) being prepared by the standard methods.

In physical properties they differ in being solids usually sparingly soluble in cold water and decomposing on distillation with loss of carbon dioxide. The carboxyl group is readily eliminated by distillation with lime.

They may be prepared by the following general reactions:

(1) Oxidation of any benzene compound with a carbon side-chain, by heating with dilute nitric acid or alkaline potassium permanganate:



Aromatic alcohols, aldehydes, ketones, etc., may of course be used as well as hydrocarbons.

(2) Fusion of a sulphonic acid with potassium formate:

$$C_6H_5SO_3K + HCOOK = C_6H_5COOH + K_2SO_3$$

(3) Hydrolysis of the corresponding cyano compound.

This may be prepared by the following methods:

(*a*) Distillation of a sulphonic acid with potassium cyanide:

$$C_6H_5SO_3K + KCN = C_6H_5CN + K_2SO_3$$

(*b*) The Sandmeyer reaction, by treating a diazotised amine with hot cuprous cyanide (or $KCu(CN)_2$):

$$2\,C_6H_5N_2Cl + Cu_2(CN)_2 = 2\,C_6H_5CN + Cu_2Cl_2 + 2\,N_2$$

(*c*) In the side chain by boiling a side-chain halide with alcoholic potassium cyanide:

$$C_6H_5CH_2Cl + KCN = C_6H_5CH_2CN + KCl$$

(4) By the Friedel and Crafts reaction, using carbonyl chloride and treating the resulting acid chloride with water:

$$C_6H_5H + Cl.COCl \xrightarrow{AlCl_3} C_6H_5COCl + HCl$$

(5) By hydrolysis of the corresponding benzo-trichloride:

$$C_6H_5CCl_3 + 3\,KOH \longrightarrow [C_6H_5C(OH)_3] \longrightarrow C_6H_5COOH$$

Several other methods are used for the preparation of nuclear and side-chain hydroxy acids and unsaturated acids (cf. **Perkin and Kolbe reactions**).

### Mono-Carboxylic Acids

**Benzoic acid,** $C_6H_5COOH$, occurs naturally in the free state and the benzyl ester in **gum benzoin** and **Peru balsam.** It also occurs as **hippuric acid** (benzoyl glycine) in the urine of herbivorous animals. It is prepared commercially from toluene by conversion of this into benzotrichloride and subsequent hydrolysis by heating under pressure with milk of lime. On acidification the free acid is precipitated, filtered and purified by recrystallisation from boiling water or by sublimation.

Benzoic acid is a crystalline solid melting at 121°. It is almost insoluble in cold water but readily soluble in hot water and in organic solvents. It dissolves readily in alkalis and alkaline carbonates.

A neutral solution of a benzoate gives with ferric chloride a light yellow precipitate of **ferric benzoate,** soluble in acids.

On nitration, etc., it yields meta-substituted compounds (cf. Crum Brown and Gibson's Rule). Ortho and para derivatives are usually prepared by oxidising the corresponding substituted toluenes.

**Benzoic Esters.**—These are prepared in the usual way by boiling a mixture of benzoic acid, the alcohol and a little concentrated sulphuric acid for some hours, pouring into water

and separating or extracting with ether. They are colourless liquids with a peculiar characteristic aromatic odour. Ethyl benzoate boils at 211°.

**Benzoyl chloride,** $C_6H_5COCl$, is prepared by mixing equimolecular proportions of benzoic acid and phosphorus pentachloride and fractionally distilling the product:

$$C_6H_5COOH + PCl_5 = C_6H_5COCl + HCl + POCl_3$$

Benzoyl chloride is a heavy liquid boiling at 197°, the vapour having an unpleasant smell and attacking the eyes.

It resembles benzene sulphonic chloride in being very slowly attacked by cold water, more readily by hot water, and fairly rapidly by alkalis.

**Benzoic anhydride,** $(C_6H_5CO)_2O$, is prepared by heating benzoyl chloride with sodium benzoate. It is a white solid melting at 42°.

**Benzamide,** $C_6H_5CONH_2$, may be prepared by any of the standard methods, *e.g.* by heating ammonium benzoate to 200°, by heating benzoic esters with ammonia, etc. It is best prepared by grinding benzoyl chloride with ammonium carbonate in a mortar and extracting the product with cold water in which benzamide is insoluble.

Benzamide is a white crystalline solid soluble in hot water and melting at 128°. It is readily hydrolysed by boiling acids or alkalis.

**Benzonitrile,** $C_6H_5CN$, may be prepared by distilling benzamide with phosphoric anhydride, by fusing potassium benzene sulphonate with potassium cyanide, or, best, by the Sandmeyer reaction from benzene diazonium chloride and cuprous cyanide.

It is a colourless liquid insoluble in water and boiling at 191°. Its odour resembles those of nitrobenzene and benzaldehyde. As a nitrile it undergoes hydrolysis in the normal manner to benzoic acid.

**Phenylacetic acid,** α-toluic acid, $C_6H_5CH_2COOH$, is isomeric with the toluic acids and is prepared by the hydrolysis of benzyl cyanide, which is made by boiling benzyl chloride

with an alcoholic suspension of potassium cyanide. It is a white solid melting at 77°.

**Mandelic acid,** $C_6H_5CHOH.COOH$, is formed when **amygdalin** is hydrolysed by boiling hydrochloric acid. It is prepared by hydrolysing benzaldehyde cyanhydrin (**mandelonitrile**) just as lactic acid is synthesised by the hydrolysis of acetaldehyde cyanhydrin. Like lactic acid it contains an **asymmetric carbon atom** and can therefore exist in **dextro, lævo** and **racemic** forms. The latter, which is formed from benzaldehyde cyanhydrin, melts at 118°. It may be resolved by fractional crystallisation of the cinchonine salt. The lævo and dextro forms (the former of which results from the hydrolysis of amygdalin) melt at 133°.

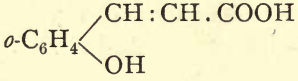
**Cinnamic acid,** $C_6H_5CH:CH.COOH$. This acid occurs as the benzyl ester in various balsams. It is prepared synthetically by the **Perkin reaction.** Benzaldehyde is boiled for several hours with anhydrous sodium acetate and excess of acetic anhydride:

$$C_6H_5CHO + H_2CH.COONa \longrightarrow C_6H_5CH:CH.COONa$$

The product is poured into dilute sodium carbonate and the excess of benzaldehyde removed by a current of steam. On acidification cinnamic acid is precipitated.

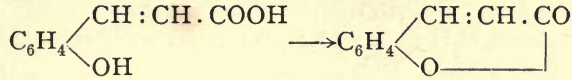
It is a white crystalline solid soluble in hot water and melting at 133°. In neutral solutions it gives a yellow precipitate with ferric chloride. As an unsaturated compound it decolorises bromine water, forming a dibromide and is reduced by sodium amalgam to hydrocinnamic acid, $C_6H_5CH_2.CH_2COOH$. On oxidation it yields benzoic acid.

**Coumarinic acid,** *o*-oxycinnamic acid,



The sodium salt is prepared by the Perkin reaction, using salicylaldehyde and sodium acetate. Coumarinic acid, however, cannot be prepared in the free state since it immediately loses

the elements of water on liberation, forming the **lactone** coumarin:

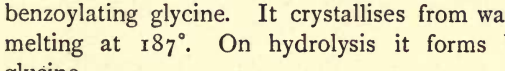


Coumarinic acid — Coumarin

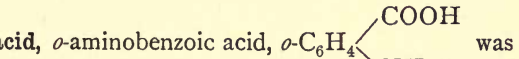
**Coumarin** is a white solid melting at 70° and possessing a fragrant odour. It is prepared as described above from salicylaldehyde. It dissolves in potash, forming potassium coumarinate, but on acidification the acid immediately loses the elements of water, reprecipitating coumarin.

**Hippuric acid,** $C_6H_5CO.NHCH_2COOH$, occurs in the urine of herbivorous animals. It may be prepared synthetically by benzoylating glycine. It crystallises from water in hard prisms melting at 187°. On hydrolysis it forms benzoic acid and glycine.

**Anthranilic acid,** *o*-aminobenzoic acid, *o*-$C_6H_4\langle^{COOH}_{NH_2}$ was first obtained by the oxidation of indigo. It is now prepared by the following series of reactions from phthalic anhydride:



Phthalic anhydride — Phthalimide



Phthalamic acid — Anthranilic acid

The hydrolysis of phthalimide to phthalamic acid and immediate oxidation are carried out in one step by the addition of bleaching powder containing lime. The action is quite analogous to the oxidation of acetamide to methylamine by sodium hypobromite.

Anthranilic acid is a white solid melting at 145°. Its alcoholic solution exhibits a faint blue fluorescence. It has the typical properties of an **amine** and a **carboxylic acid.** On diazotisation and boiling with water it forms salicylic acid. On

distillation (preferably with lime) aniline is obtained. It is used in the preparation of artificial indigo.

**Saccharin,** $C_6H_4\begin{<}{CO}{SO_2}{>}NH$, is the imide of *o*-sulphobenzoic acid. It is prepared by sulphonating toluene, isolating and oxidising the ortho acid to ortho-sulphobenzoic acid. This or its chloride on heating gives the anhydride or, in a current of ammonia, the imide.

Saccharin is a colourless crystalline solid which is of considerable value as a substitute for sugar as it is six hundred times sweeter than sugar, weight for weight. As an imide saccharin forms a sodium salt, $C_6H_4\begin{<}{CO}{SO_2}{>}NNa$, which is more frequently used than the parent substance as it is more soluble in water.

**Toluic acids,** $C_6H_4\begin{<}{CH_3}{COOH}$ may be prepared by any of the general methods (best from the tolunitriles, which are prepared from the toluidines). They are formed by regulated oxidation of the xylenes, and on further oxidation yield phthalic acids.

**Salicylic acid,** *o*-oxybenzoic acid, $o\text{-}C_6H_4\begin{<}{OH}{COOH}$ occurs naturally as the methyl ester, **oil of wintergreen.** It is prepared commercially by the **Kolbe reaction.** This consists in heating sodium phenate to 130° under pressure in a current of carbon dioxide. The first step is the formation of sodium phenyl carbonate:

$$C_6H_5ONa + CO_2 = C_6H_5O \,.\, CO \,.\, ONa$$

On raising the temperature slightly the (COONa) radical migrates to the ortho position, yielding sodium salicylate:

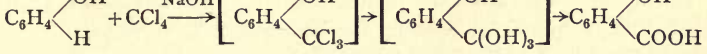
$$C_6H_4\begin{<}{OCOONa}{H} \longrightarrow C_6H_4\begin{<}{OH}{COONa}$$

Sodium phenyl carbonate — Sodium salicylate

On extraction with water and acidification salicylic acid is precipitated and is purified by crystallisation from hot water.

If the temperature is allowed to rise to 200° or if potassium phenate is used the chief product is *p*-oxybenzoic acid.

Salicylic acid may also be prepared by a slight modification of the **Reimer reaction** (p. 82), using carbon tetrachloride in place of chloroform :



Here again some *p*-oxybenzoic acid is formed.

Salicylic acid forms small colourless needles melting at 156°. It is sparingly soluble in cold water, readily in hot water, and of course in caustic soda and sodium carbonate. Solutions of the acid or its salts give a purple coloration with ferric chloride and a white precipitate with bromine water. On distillation with lime it loses carbon dioxide and yields phenol. It is best detected by the characteristic odour of *methyl salicylate* produced when the acid is heated with methyl alcohol and concentrated sulphuric acid. Salicylic acid possesses the chemical properties both of a phenol and of a carboxylic acid. It forms a neutral monosodium salt, $C_6H_4(OH)COONa$, and with excess of caustic soda an alkaline-reacting disodium salt. Owing to its phenolic character salicylic acid is largely used as a mild antiseptic. Its phenyl and β-naphthyl esters are also used for this purpose.

**Salicylic Esters.**—Those derived from the aliphatic alcohols are colourless liquids insoluble in water and possessing a characteristic odour. They dissolve in dilute caustic soda by virtue of their phenolic group and the sodium salts are somewhat sparingly soluble. On heating these salts with alkyl halides ethers are formed :

$$C_6H_4(ONa)COOCH_3 + CH_3I = C_6H_4(OCH_3)COOCH_3$$

On hydrolysis of these compounds with acid or alkali, ethers of salicylic acid are obtained :

$$C_6H_4(OCH_3)COOCH_3 + H_2O = C_6H_4(OCH_3)COOH + CH_3OH$$

**Methyl salicylate** occurs naturally as oil of wintergreen and possesses a characteristic odour. It boils at 224°.

**Phenyl salicylate,** "salol," is prepared commercially by distilling salicylic acid. Part of this loses carbon dioxide, forming phenol, which then condenses with more salicylic acid:

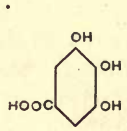
$$C_6H_4(OH).COOH = C_6H_5OH + CO_2$$
$$C_6H_4(OH).COOH + C_6H_5OH = C_6H_4(OH).COOC_6H_5 + H_2O$$

Salol, an important antiseptic, is a white crystalline solid melting at 43°. It is only hydrolysed with difficulty, boiling 70 per cent., sulphuric acid being the best reagent.

**β-Naphthyl salicylate,** "betol," is prepared by condensing β-naphthol and salicylic acid by means of a little phosphorus oxychloride. It melts at 132° and is used as an antiseptic.

**p-Oxybenzoic acid** is prepared by the **Kolbe reaction,** using potassium phenate at 200°. It is a sandy white powder melting at 210° with decomposition into phenol and carbon dioxide. It gives no colour with ferric chloride, but with bromine water tribromophenol is precipitated and carbon dioxide liberated.

**Anisic acid,** $p$-$C_6H_4(OCH_3).COOH$, the methyl ether of p-oxybenzoic ester, is prepared by oxidising anethole or anisaldehyde or it can be prepared by heating the sodium salt of methyl p-oxybenzoate with methyl iodide and hydrolysing the resulting methyl anisate. Anisic acid is a white crystalline solid melting at 184°.

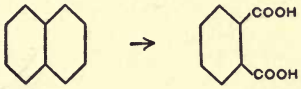
**Gallic acid,** 

occurs in gall nuts. It is best prepared by hydrolysing tannin with hydrochloric acid. It crystallises in needles and its solution gives a dark blue coloration with ferric chloride. This coloured solution forms the basis of ordinary ink.

### Dibasic Acids

The **phthalic acids** are the only important members of this series. They are prepared by the oxidation of benzene compounds with two carbon side-chains.

**Phthalic acid,** $o\text{-}C_6H_4\begin{<}COOH\\COOH\end{>}$, may be prepared by the oxidation of *o*-xylene. In practice it is invariably prepared by the oxidation of **naphthalene**:




Naphthalene

The operation is carried out by heating naphthalene to 200° with concentrated sulphuric acid containing a trace of mercuric sulphate as a catalytic oxygen carrier. The sulphuric acid is reduced to sulphur dioxide and **phthalic anhydride** sublimes over. This may be converted into the acid by boiling with water.

Phthalic acid forms small plates melting indefinitely at about 210° with loss of water and formation of phthalic anhydride. It is somewhat sparingly soluble in cold water though much more soluble than the monocarboxylic acids. Its neutralised solution gives a light yellow precipitate with ferric chloride.

On sublimation phthalic acid is readily decomposed into its anhydride.

**Phthalyl chloride,** $C_6H_4\begin{<}CCl_2\\CO\end{>}O$, is prepared by heating phthalic acid or anhydride with phosphorus pentachloride. Despite the unusual type of formula it reacts as a true acid chloride, fuming in moist air yielding phthalic acid and hydrochloric acid. The constitution is proved by the formation of **phthalide** on reduction.

**Phthalic anhydride,** $C_6H_4\begin{<}CO\\CO\end{>}O$, is prepared by the action of heat on phthalic acid. It sublimes in long needles melting at 128°. It dissolves in warm sodium hydroxide or carbonate, forming sodium phthalate. It is best characterised by heating it with resorcinol and a drop of strong sulphuric acid and dissolving the product in alkali when **fluorescein** is obtained.

If phthalic anhydride or phthalyl chloride are reduced with zinc dust and acetic acid, **phthalide**, $C_6H_4\begin{<}\begin{matrix}CH_2\\CO\end{matrix}\begin{>}O$, is obtained.

**Phthalimide**, $C_6H_4\begin{<}\begin{matrix}CO\\CO\end{matrix}\begin{>}NH$, is prepared by heating phthalic anhydride in a stream of ammonia:

$$C_6H_4\begin{<}\begin{matrix}CO\\CO\end{matrix}\begin{>}O + NH_3 = C_6H_4\begin{<}\begin{matrix}CO\\CO\end{matrix}\begin{>}NH + H_2O$$

It is a white crystalline solid melting at 230° and is insoluble in water; but being an imide, it dissolves in caustic potash, forming a potassium salt.

**Potassium phthalimide**, $C_6H_4\begin{<}\begin{matrix}CO\\CO\end{matrix}\begin{>}NK$, is best prepared by mixing alcoholic solutions of phthalimide and potassium hydroxide when the potassium salt is precipitated as a white solid easily soluble in water. It is an important reagent in synthetical chemistry for the preparation of primary amines. If heated for a short time with almost any halogen compound (except nuclear halides such as chlorobenzene) a potassium halide and a substituted phthalimide are produced which may be separated by extraction with water. The phthalimide derivative on hydrolysis with alcoholic potash or concentrated hydrochloric acid yields phthalic acid and an amine:

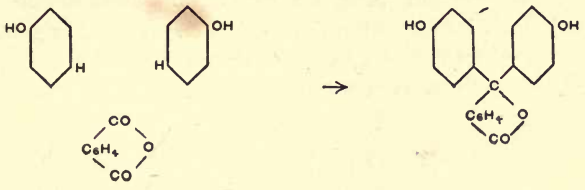
$$C_6H_4\begin{<}\begin{matrix}CO\\CO\end{matrix}\begin{>}NK + RX(X = \text{halogen}) = C_6H_4\begin{<}\begin{matrix}CO\\CO\end{matrix}\begin{>}NR + KX$$

$$C_6H_4\begin{<}\begin{matrix}CO\\CO\end{matrix}\begin{>}NR + 2\,H_2O = C_6H_4(COOH)_2 + RNH_2$$

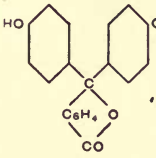
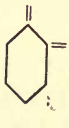
**The Phthaleins.**—These important colouring matters are prepared by condensing phenols with phthalic anhydride by heating with a little sulphuric acid or zinc chloride.

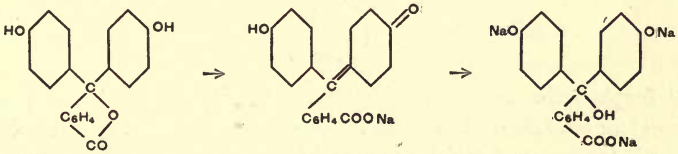
**Phenol-phthalein** is prepared in this way from phenol and phthalic anhydride. It is a white powder soluble in alcohol.

It dissolves in caustic alkalis yielding intensely red solutions, but if the alkali is concentrated the colour rapidly vanishes.



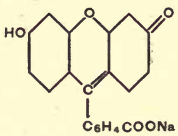
Phenol-phthalein, colourless

The mono-sodium salt of this phenol should presumably possess the formula  , but there is obviously no reason why a substance of this constitution should have such an intense colour. It has been suggested that all highly coloured substances possess a structure similar to that of *o*- **or** *p*-**quinone** (themselves intensely coloured substances), *i.e.* contain the grouping or  . Though there are exceptions to this theory it agrees very well with a large number of facts. Practically every dyestuff can be written with a quinonoid structure and when this structure is impossible the substance very rarely possesses more than a slight colour. Applying this "**quinonoid theory**" to the colour changes of phenol-phthalein with caustic soda we have



Phenol-phthalein, colourless | Mono-sodium salt, red | Tri-sodium salt, colourless

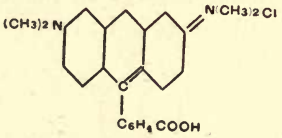
**Fluorescein,** resorcinol-phthalein, is made in exactly the same way as phenol-phthalein, using resorcinol in place of phenol (p. 96). Fluorescein itself is a pale yellow solid dissolving in acidified alcohol to a pale yellow solution. On adding a little alkali a magnificent green fluorescence appears which is removed by acid. The fluorescent solution contains the compound




Fluorescein is occasionally used in dyeing to impart a "shot" appearance to a fabric which is afterwards dyed with some other colouring matter, since fluorescein is practically useless as a dyestuff.

Tetrabromo and tetra-iodo fluoresceins are used for the same purpose as fluorescein under the names of "*eosin*" and "*erythrosin*" respectively. They are prepared by direct substitution, using aqueous or alcoholic solutions of the halogen and of fluorescein.

**The Rhodamines.**—These dyestuffs are condensation products of phthalic anhydride and *m*-aminophenols. They are light red solids dissolving in acids to form intensely red fluorescent solutions. The most important, **Rhodamine G,** is prepared from phthalic anhydride and dimethyl *m*-aminophenol just as fluorescein is prepared from resorcinol. Its fluorescent red hydrochloride has the quinonoid formula:




**Isophthalic acid,** $m$-$C_6H_4(COOH)_2$, is prepared by the complete oxidation of *m*-xylene with dilute nitric acid or chromic acid. It does not yield an anhydride but melts and sublimes above 300°.

**Terephthalic acid,** $p$-$C_6H_4(COOH)_2$, is prepared by oxidising $p$-xylene, $p$-cymene, and many of the terpenes which are hydro-derivatives of $p$-cymene. Terephthalic acid does not melt nor give an anhydride but sublimes at a high temperature. It is also characterised by its insolubility in all ordinary organic solvents.

**Mellitic acid,** $C_6(COOH)_6$, occurs in peat as the aluminium salt "honeystone." This is also obtained when graphite is oxidised with potassium permanganate. Mellitic acid crystallises in needles and cannot be nitrated or sulphonated.

## CHAPTER XIV

### MULTINUCLEAR HYDROCARBONS

**DIPHENYL**, $C_6H_5 . C_6H_5$, may be prepared by the Fittig reaction, by heating an ethereal solution of bromobenzene with sodium. It is best prepared by passing benzene vapour through a red-hot tube:

$$2\,C_6H_6 = C_6H_5 . C_6H_5 + H_2$$

It forms colourless plates melting at 71°.

The only important derivative of diphenyl is **benzidine**, which has been previously described (p. 49). Benzidine may be prepared from diphenyl by nitration and reduction:

$$C_6H_5—C_6H_5 \longrightarrow NO_2 . C_6H_4—C_6H_4 . NO_2 \longrightarrow NH_2 . C_6H_4—C_6H_4 . NH_2$$

**Diphenylmethane**, $CH_2(C_6H_5)_2$, is best prepared by the Friedel and Crafts' reaction from benzyl chloride, benzene and aluminium chloride:

$$C_6H_5CH_2Cl + C_6H_6 = C_6H_5CH_2C_6H_5 + HCl$$

It is a colourless solid melting at 26° and possessing an aromatic odour. On oxidation it yields progressively benzhydrol, benzophenone and benzoic acid.

**Triphenylmethane**, $CH(C_6H_5)_3$, is prepared by the Friedel and Crafts' reaction, using chloroform and benzene or benzal chloride and benzene. The former method is more usually employed:

$$CHCl_3 + 3\,C_6H_6 = CH(C_6H_5)_3 + 3\,HCl$$
$$C_6H_5CHCl_2 + 2\,C_6H_6 = CH(C_6H_5)_3 + 2\,HCl$$

Triphenylmethane forms colourless prisms melting at 94° and is of theoretical importance as the parent hydrocarbon of the **triphenylmethane dyestuffs**, the chief of which is magenta.

On treatment with bromine triphenylmethane yields triphenylmethyl bromide, $(C_6H_5)_3CBr$, which is hydrolysed by boiling water to triphenycarbinol.

**Triphenylcarbinol**, $(C_6H_5)_3COH$, a white crystalline solid melting at 159°. This may also be prepared by the direct oxidation of triphenylmethane with chromic acid or by the Grignard reaction from benzophenone and magnesium phenyl bromide:

$$(C_6H_5)_2CO + MgC_6H_5Br \longrightarrow (C_6H_5)_2C\begin{matrix}OMgBr\\C_6H_5\end{matrix} \xrightarrow{H_2O} (C_6H_5)_3COH + Mg(OH)Br$$

The magenta dyestuffs are hydrochlorides of aminotriphenylcarbinols. Triphenylcarbinol dissolves in concentrated sulphuric acid, forming an intensely yellow solution.

# CHAPTER XV

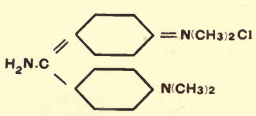
## THE DI- AND TRIPHENYLMETHANE DYES

### Diphenylmethane Colours

THE chief dyestuff derived from diphenylmethane is auramine, which is an important yellow colouring matter.

**Auramine** is prepared by heating **Michler's ketone** (p. 84) with zinc chloride in a current of ammonia :

$$CO(C_6H_4NMe_2)_2 + NH_3 \longrightarrow C(=NH)(C_6H_4NMe_2)_2$$

The intense colour is only produced when the base is dissolved in acid and the salt therefore probably possesses the quinonoid formula,  (p. 97).

### Triphenylmethane Colours

The constitutions of these dyestuffs and their chief derivatives are most easily deduced from a study of rosaniline (magenta, fuchsine) and para-rosaniline, the first dyestuffs of this series to be isolated and investigated.

**Rosaniline** (magenta) was originally prepared by boiling crude aniline (from benzene containing toluene) with an oxidising agent. Arsenic acid was first used as an oxidant, but owing to its poisonous nature it has been replaced by nitrobenzene. The

oxidation product on extraction with dilute hydrochloric acid yields a bright red solution which deposits rosaniline hydrochloride as green crystals with a metallic reflex. This substance possesses the formula $C_{20}H_{20}N_3Cl$. Rosaniline is only obtained from a mixture of aniline and *o*- and *p*-toluidines. If no *o*-toluidine is present a similar dyestuff, **para-rosaniline**, is obtained which possesses the formula $C_{19}H_{18}N_3Cl$. Both aniline and *p*-toluidine are essential for the production of a red dyestuff. It is therefore obvious that rosaniline is a *methyl homologue* of para-rosaniline.

Para-rosaniline solution on treatment with one equivalent of caustic potash is slowly decolorised and a colourless "**carbinol**" **base**, $C_{19}H_{18}N_3(OH)$, is precipitated. This is readily reduced to a **leuco-base**, $C_{19}H_{19}N_3$, which from analysis of its acetyl derivative and platinichloride is found to contain three $NH_2$ groups and may therefore be written $C_{19}H_{13}(NH_2)_3$. These groups may be eliminated by diazotisation and subsequent boiling with alcohol, the resulting hydrocarbon possessing the formula $C_{19}H_{16}$. Fischer recognised this substance as **triphenylmethane**, $CH(C_6H_5)_3$. Starting from this hydrocarbon Fischer reversed the above process according to the following scheme and succeeded in synthesising para-rosaniline:

$$CH(C_6H_5)_3 \xrightarrow{HNO_3} CH(C_6H_4NO_2)_3 \xrightarrow{SnCl_2} \underset{\text{Leuco-base}}{CH(C_6H_4NH_2)_3}$$

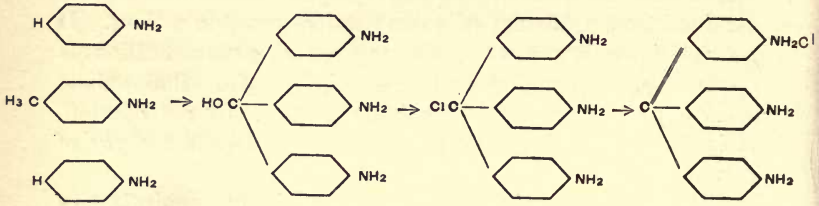
$$\xrightarrow{PbO_2} \underset{\text{Carbinol base}}{C(OH).(C_6H_4NH_2)_3} \xrightarrow{HCl} \underset{\text{Para-rosaniline}}{CCl(C_6H_4NH_2)_3}$$

The above formula for para-rosaniline, though agreeing with the analytical results, gives no explanation of the intense colour and is therefore better written in the **quinonoid form**:

$$\begin{array}{l} \quad\quad C_6H_4{=}NH_2Cl \\ C \\ \quad\quad C_6H_5NH_2 \end{array}$$

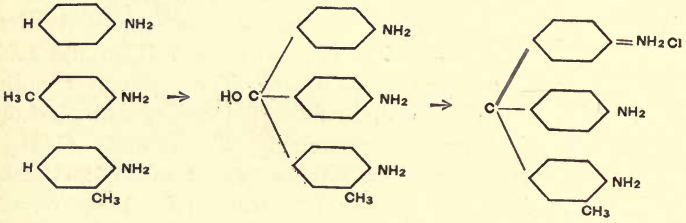
It has subsequently been proved and may here be assumed that the amino groups are all in the *para* position to the central "methane" carbon linking (p. 107).

The formation of para-rosaniline and of rosaniline therefore evidently takes the following course, the methyl group of the para-toluidine forming the "methane" carbon atom:




Para-rosaniline

and




Rosaniline

**Aniline Blue.**—This dyestuff is derived from para-rosaniline by the conversion of each $NH_2$ group into $NHC_6H_5$. As with the azo-dyes the shade deepens as the molecular weight of the substance increases. The actual *phenylation* is carried out by boiling para-rosaniline with aniline for several hours in the presence of a trace of benzoic acid. (The function of the latter is unknown.)

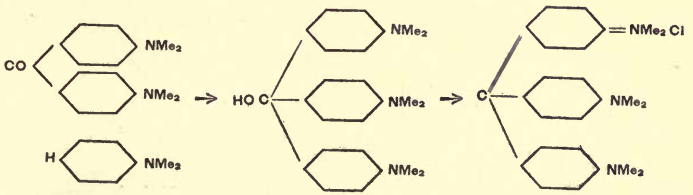
Aniline blue is insoluble in water but soluble in alcohol, and is therefore known commercially as *spirit blue.* To render it soluble in water it is sulphonated, the resulting sulphonic acids being known as *Nicholson's Blue*, *Water Blue*, *Navy Blue* or *Alkali Blue.*

**Methyl Violet** is derived from para-rosaniline by methylating the amino groups and is probably a mixture of various methyl derivatives. The preparation was originally carried out by Hofmann, who used methyl iodide as the methylating agent, and

the dyestuff thus produced was known as *Hofmann's Violet.* The cost of methyl iodide, however, prevented these colours from being of any commercial value.

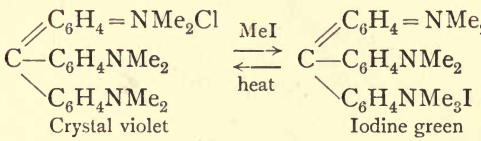
Methyl violet is now prepared by the oxidation of dimethylaniline by mixing it with some indifferent solid together with a trace of copper chloride as an oxygen carrier, heating and exposing the mass to air. The mechanism of the reaction is not definitely known.

**Crystal Violet** is the only methylated rosaniline of definitely known constitution, each amino group being completely methylated. It is prepared by heating dimethylaniline with Michler's ketone in the presence of phosphorus oxychloride:




Crystal violet

If crystal violet is warmed with methyl iodide one of the $NMe_2$ groups is converted into $NMe_3I$, the resulting substance being a green dyestuff **Iodine Green.** It is of no practical importance since it readily dissociates again on heating, evolving methyl iodide and leaving crystal violet:

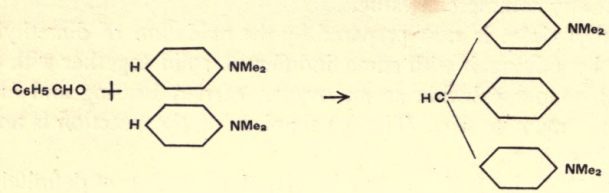



Crystal violet — Iodine green

**Malachite Green** is perhaps the simplest dyestuff of the triphenylmethane series. It is prepared by condensing benzaldehyde and dimethylaniline at 150° with zinc chloride.

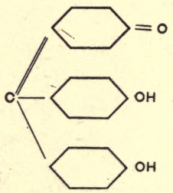
The resulting colourless **leuco base** is oxidised to the **carbinol base** by means of lead peroxide and the carbinol base is dissolved in hydrochloric acid (forming the dyestuff) and precipi-

tated as the double zinc salt by the addition of a solution of zinc chloride:




Malachite green

**Aurine**, rosolic acid, is the chief oxytriphenylmethane. It is a yellow dyestuff, now of little importance. Its constitution follows from its synthesis from para-rosaniline by diazotisation of the amino groups. On boiling the diazo compound with water *aurine* is produced and consequently has the formula:



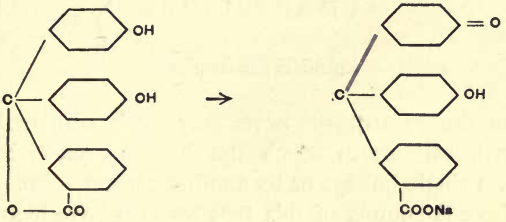

If aurine is heated with ammonia under pressure, para-rosaniline is reproduced.

Aurine is prepared commercially by heating phenol with oxalic acid, which supplies the methane carbon atom.

It dissolves in alkalis, yielding a red solution.

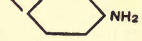
**The Phthaleins**, strictly speaking, are triphenylmethane derivatives, but they have been described in connection with phthalic acid.

The triphenylmethane structure is perhaps more apparent if the formulæ of phenol-phthalein and its red sodium salt are written as follows:




## Proof of the Constitution of Para-rosaniline

The previously indicated proof that para-rosaniline is a derivative of triaminotriphenyl carbinol contains no evidence as to the positions of the amino groups in the phenyl nuclei. The proof may readily be rendered complete by the addition of the following evidence:

If benzaldehyde is condensed with aniline in the presence of concentrated sulphuric acid a diamino-triphenylmethane is obtained. This on diazotisation in warm solution yields the corresponding dioxy-triphenylmethane, which on fusion with potash yields *p.p.*-dioxy-benzophenone. The original condensation product must therefore possess the formula $C_6H_5CH$ 


If the benzaldehyde be replaced by *p*-nitrobenzaldehyde the condensation product on reduction yields para-leucaniline.

All the amino groups in the latter substance must therefore be in the para position to the "methane" carbon atom.

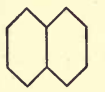
## CHAPTER XVI

### NAPHTHALENE

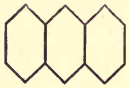
UP to the present we have only dealt with multinuclear hydrocarbons in which the benzene nuclei have been united by a single linkage or by another carbon atom.

Besides compounds of this type we may have hydrocarbons which contain two or more benzene nuclei united by carbon atoms common to both.

The chief types of such **condensed nuclei** are

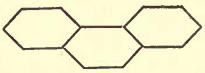


Naphthalene



Anthracene

and



Phenanthrene

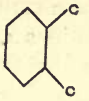
#### The Constitution of Naphthalene

The empirical formula of naphthalene obtained from analytical results is $C_5H_4$, and vapour density determinations show the molecular formula to be $C_{10}H_8$.

The chemical properties of naphthalene and its derivatives strongly resemble those of the analogous benzene compounds.

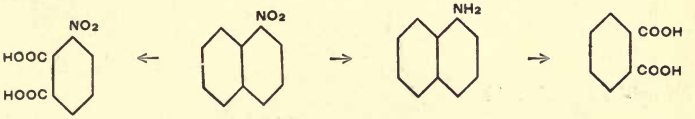
For example, naphthalene can be nitrated, chlorinated and sulphonated, and will undergo the Friedel and Crafts' condensations. The amino and hydroxy compounds also strongly resemble aniline and phenol in properties. We may therefore conclude that naphthalene is similar in structure to benzene.

Oxidation of naphthalene by the ordinary methods (preferably

by concentrated sulphuric acid at 300°) yields **phthalic acid**, showing that naphthalene contains the grouping 

The existence of two benzene nuclei is shown in the following way:

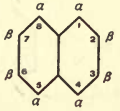
Naphthalene on nitration yields a mononitro-derivative which on oxidation yields **nitrophthalic acid**, the un-nitrated ring being broken down. If the nitronaphthalene is reduced to **amino-naphthalene**, this on oxidation yields not aminophthalic acid but **phthalic acid**. The portion of the naphthalene molecule containing the nitro group is by the first experiment proved to contain a benzene nucleus and the second experiment shows that the unsubstituted portion also contains this nucleus. The only way of writing $C_{10}H_8$ to satisfy these facts is to assume the condensed nucleus :




As regards the disposal of the carbon valencies the same difficulties are met with as in the case of benzene and the same two types of formula may be adopted.

Both these formulæ explain the formation of the various addition compounds derived from naphthalene, such as di-, tetra- and deca-hydro compounds.

### Nomenclature of Naphthalene Derivatives

The naphthalene ring is usually lettered or numbered as follows: 

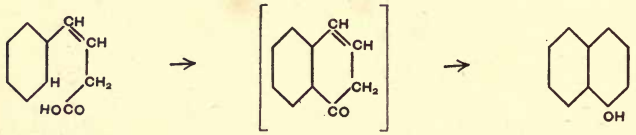
the carbon atoms adjacent to the junction of the benzene nuclei being the $\alpha$ carbon atoms and those remote the $\beta$ carbon atoms. The positions 1.8 and 4.5 are known as the **peri** positions.

It is obvious that the positions 1, 4, 5 and 8 are equivalent and also the positions 2, 3, 6 and 7. It therefore follows that two mono-derivatives can be derived from naphthalene, an $\alpha$ and a $\beta$ compound.

### Syntheses of Naphthalene

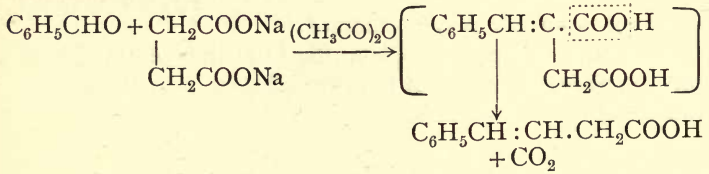
There are not many examples of the synthesis of the naphthalene ring, but they are all in accord with the accepted formula of naphthalene.

(1) The most important, perhaps, is the synthesis of **$\alpha$-naphthol** discovered by Fittig. This substance results by loss of water and rearrangement when **phenyl-isocrotonic** acid is heated:

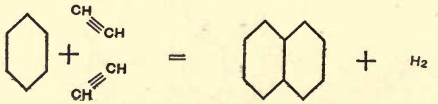



Phenyl-isocrotonic acid

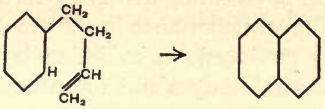
Phenyl-isocrotonic acid is prepared by the Perkin synthesis as follows:




(2) If a mixture of benzene and acetylene is passed through a red-hot tube naphthalene and hydrogen are produced:



(3) If **phenylbutylene** is heated to redness a similar reaction takes place:

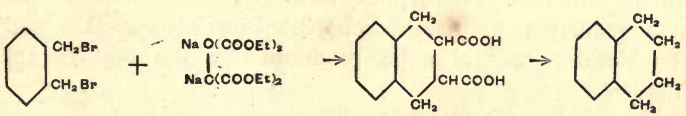


Phenylbutylene

Phenylbutylene is prepared from benzylchloride, allyl iodide and sodium:

$$C_6H_5CH_2Cl + ICH_2 . CH = CH_2 + 2\,Na = C_6H_5CH_2 . CH_2 . CH = CH_2 + NaI + NaCl$$

(4) ***o*-Xylylene dibromide** condenses with sodio-ethanetetracarboxylic ester, and the resulting carboxylic ester on hydrolysis and distillation with lime yields tetrahydronaphthalene:



**Naphthalene,** $C_{10}H_8$, occurs to a large extent in the middle oil from coal tar (b.p. 170–220°). It crystallises from the oil on standing and is separated from the phenolic liquid portion by straining. The crude naphthalene is then pressed to separate as much oil as possible and heated with a little concentrated sulphuric acid. The impurities are sulphonated and can be readily dissolved out by water and the purified naphthalene is finally distilled alone or in steam, when a pure product is obtained.

Naphthalene is a white crystalline solid insoluble in water, melting at 80° and boiling at 218°. It is readily volatile, even at ordinary temperatures, and therefore is contained in appreciable quantities in coal gas. It burns with a smoky flame and is sometimes used for enriching coal gas which possesses a poor illuminating power.

Naphthalene possesses a characteristic tarry odour and is

largely used as a mild antiseptic and as a vermicide (particularly for preserving fur). It is also a very important starting material for the preparation of colouring matters. Its hydroxy and amino derivatives are of great importance in the azo dye industry, while the phthalic acid produced on oxidation is the source of the phthalein and rhodamine dyes and of anthranilic acid (for synthetic indigo).

Naphthalene may be readily characterised by the formation of its **picrate**, a double compound which crystallises in long yellow needles (m.p. 149°) when alcoholic solutions of naphthalene and picric acid are mixed.

On its chemical properties naphthalene resembles benzene, the nitro-, chlor-, sulphonic- etc. derivatives closely resembling their benzene analogues.

On reduction with sodium and amyl alcohol naphthalene is converted into tetrahydronaphthalene, one benzene nucleus becoming saturated. With phosphorus and hydriodic acid complete reduction to decahydronaphthalene ensues. Di- and tetrachlorides may also be produced by the addition of chlorine.

**Naphthalene Homologues.** These compounds, which are of no practical importance, occur in small amounts in coal tar. They are prepared synthetically by the Fittig or Friedel and Crafts' reactions.

**Halogen Compounds.** The α-chlor and α-brom derivatives may be prepared by direct substitution or by the diazo reaction from the α-amino compound. The β isomers can only be obtained by the latter method from β-naphthylamine.

**α-Chloronaphthalene** boils at 263° and **α-Bromonaphthalene** at 279°. They are heavy liquids resembling chloro- and bromobenzene in properties.

**Nitro Compounds.** Nitration of naphthalene gives rise to **α-nitronaphthalene**, a yellow odourless crystalline solid melting at 61°. Further nitration yields a mixture of 1.5 and 1.8 dinitroderivatives.

**β-Nitronaphthalene** cannot be obtained by direct nitration. It is prepared by a modification of the Sandmeyer reaction.

β-Naphthylamine is diazotised and the solution treated with a mixture of sodium nitrite and cuprous oxide. This appears to react as cuprous nitrite and the $NH_2$ group is replaced by $NO_2$. This method appears to be of general application for the preparation of nitro compounds.

**Sulphonic Acids.**—These are prepared and isolated by the method described for benzene sulphonic acid.

If the temperature of sulphonation is kept at 80° the **α-sulphonic** acid is produced, but at 160° only the **β compound** is formed. By altering the temperature, time and strength of acid a number of di- and trisulphonic acids may be prepared. These polysulphonic acids are of commercial importance as on fusion with caustic potash they yield naphthol sulphonic acids, which are largely used in the azo dye industry.

### Naphthylamines

**α-Naphthylamine** is prepared from α-nitronaphthalene by reduction with iron and hydrochloric acid and from α-naphthol by heating under pressure with the compound of calcium chloride and ammonia. This latter method is extensively used in the naphthalene series, though with benzenoid compounds the yields are so poor that this method is very rarely used.

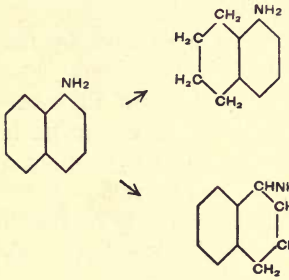
α-Naphthylamine forms colourless needles melting at 50°, boiling at 300° and possessing an unpleasant odour. It possesses all the usual properties of a primary aromatic amine. Its hydrochloride is sparingly soluble in cold water.

**β-Naphthylamine** cannot be prepared from β-nitronaphthalene since it is the source of the latter substance. It is prepared commercially by heating β-naphthol under pressure with ammonia and calcium chloride. It is a colourless, odourless solid melting at 112°.

On reduction with sodium and amyl alcohol each naphthylamine yields two isomeric tetrahydro compounds. One of these possesses the usual reactions of a primary aromatic amine, *i.e.* is a weak base and can be readily diazotised. The other reacts as a primary aliphatic amine, being a strong base with an

ammoniacal odour and reacting with nitrous acid in the cold evolving nitrogen.

Bamberger has assigned the following formulæ to these compounds :




$NH_2$ group in benzenoid ring, therefore reacts as an aromatic amine

$NH_2$ group in non-benzenoid ring, therefore reacts as an aliphatic amine

### Naphthylamine Sulphonic Acids

A large number of these acids have been prepared and many are used in the azo dye industry. The most important is naphthionic acid, the naphthalene analogue of sulphanilic acid.

**Naphthionic acid,** $C_{10}H_6\begin{cases}NH_2\,(1)\\SO_3H\,(4)\end{cases}$ is prepared by heating α-naphthylamine with ordinary concentrated sulphuric acid at 130° until a test portion is completely soluble in alkali. Naphthionic acid is a white infusible solid soluble in alkalis but sparingly soluble in water or acids. A large number of azo dyes are derived from its diazo compound.

### Naphthols

**α-Naphthol** is prepared from naphthalene and sulphonic acid by fusion with potash. It is a white crystalline solid melting at 94° and possessing a characteristic somewhat unpleasant odour. It is almost insoluble in cold water but dissolves in hot water, caustic alkalis and the usual organic solvents. With ferric chloride it gives a violet precipitate of α-dinaphthol.

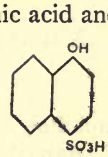
**β-Naphthol** is prepared in the same way as the α compound from naphthalene β-sulphonic acid. It closely resembles α-naphthol in properties but melts at 122° and gives a greenish-white *dinaphthol* with ferric chloride. The methyl ether prepared by warming β-naphthol with caustic soda and methyl iodide is known as **nerolin** and has a very characteristic odour.

On reduction the naphthols behave in the same way as the naphthylamines, two tetrahydro compounds being obtained, one of which reacts as a phenol and the other as a secondary alcohol.

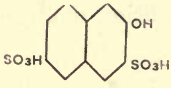
### Naphthol Sulphonic Acids

A large number of these are of technical importance. They are prepared by sulphonation of the naphthols, by regulated fusion of polysulphonic acids with potash or by diazotisation of naphthylamine sulphonic acids.

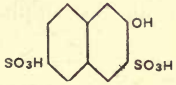
The three most important are **Neville and Winther's** acid, **R acid** and **G acid.** The first is 1 naphthol 4 sulphonic acid and is prepared from naphthionic acid by diazotisation:




R acid and G acid are β-naphthol disulphonic acids:




R acid, 2.3.6

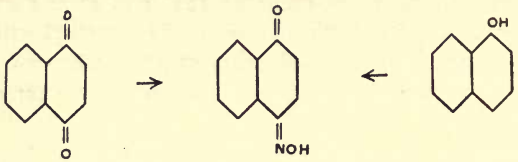



G acid, 2.6.8

### Nitrosonaphthols

α-Naphthol reacts with nitrous acid in dilute aqueous solution, yielding a mixture of 2. and 4. nitroso-α-naphthols. These compounds on oxidation yield nitro-α-naphthols and on reduction

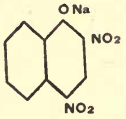
amino-α-naphthols. They are tautomeric forms of the corresponding naphthoquinone monoximes:




**α-Nitroso-β-naphthol** is best prepared by boiling alcohol solutions of β-naphthol and zinc chloride with careful addition of sodium nitrite. A red zinc salt of α-nitroso-β-naphthol separates and can be converted into the green sodium salt and hence into the free nitrosonaphthol. This is a brown crystalline solid melting at 106°. Mordanted with ferrous sulphate it is used as a dyestuff, **Naphthol Green.**

### Nitronaphthols

Two of these are important yellow dyestuffs.

**Martius' Yellow,** 

, the sodium salt of dinitro-α-naphthol, is prepared by the direct nitration of α-naphthol.

**Naphthol Yellow** is the 7. sulphonic acid of Martius' Yellow and is prepared by the nitration of α-naphthol-2.4.7.-trisulphonic acid, two sulphonic groups being replaced by nitro groups.

### Naphthoquinones

**α-Naphthoquinone,**

, the analogue of benzoquinone, is prepared by the direct oxidation of naphthalene by a boiling

solution of chromic anhydride in acetic acid. It is also formed by the oxidation of α-naphthylamine, naphthionic acid, or 4 amino-α-naphthol with potassium dichromate. Its monoxime is identical with α-nitroso-α-naphthol. α-Naphthoquinone possesses all the typical properties of a quinone. It forms yellow crystals, is volatile in steam, sublimes readily, is reduced by sulphur dioxide and possesses a pungent irritating odour.

**β-Naphthoquinone,** , is prepared by oxidising 2 amino 1 naphthol with ferric chloride. It is non-volatile, odourless and is unattacked by sulphur dioxide, and therefore is probably not a true quinone but simply an *ortho* diketone (cf. anthraquinone).

**Naphthoic Acids.**—These are the monocarboxylic acids of naphthalene and the analogues of benzoic acid, which they strongly resemble in physical and chemical properties.

They may be prepared by the general methods given for benzoic acid. In practice they are made from the nitriles, which in turn are best prepared from the naphthylamines by the Sandmeyer reaction.

## CHAPTER XVII

### ANTHRACENE AND PHENANTHRENE

ANTHRACENE occurs to a comparatively small extent in the "**anthracene oil,**" (b.p. 270–360°) from coal tar, but in spite of the difficulty of isolation and consequent high price it is of great commercial importance as the source of **alizarin** and the allied dyestuffs.

If the crude anthracene oil is allowed to stand for several weeks it deposits nearly all its anthracene together with phenanthrene, carbazole, etc., as a slimy green solid containing about 15 per cent. of anthracene. This is roughly separated from the liquid and freed from adherent oil by pressing it in canvas bags. Many methods are in use for the further purification of the anthracene from phenanthrene and carbazole. The methods most generally employed consist in washing the crude anthracene with **solvent naphtha** or **pyridine bases,** in which anthracene is almost insoluble. This treatment yields a product containing 50 to 60 per cent. of anthracene and is worked up without further purification.

Pure anthracene may be prepared by further extractions with carbon disulphide in which phenanthrene is easily soluble and finally by sublimation or crystallisation from benzene.

**Anthracene,** $C_{14}H_{10}$, forms white, odourless plates with a blue fluorescence. It melts at 213°, boils at 350° and readily sublimes. It is somewhat sparingly soluble in ordinary organic solvents.

It may be characterised by means of its **picrate,** which separates in red needles (m.p. 138°) when acetic acid or benzene solutions of anthracene and picric acid are mixed.

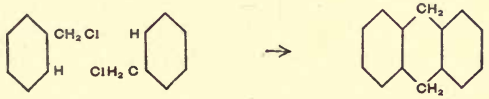
In chemical properties anthracene is a typical aromatic hydrocarbon. On reduction with sodium and alcohol it readily yields **dihydroanthracene**. By the action of hydriodic acid the benzene rings are reduced, $C_{14}H_{16}$ and $C_{14}H_{24}$ being finally obtained.

On oxidation with chromic acid anthracene yields **anthraquinone**, $C_{14}H_8O_2$. Anthracene cannot be directly nitrated, since nitric acid oxidises it to anraquinone.

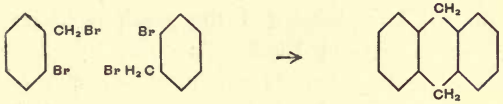
### Syntheses of Anthracene

The constitutions of anthracene and anthraquinone are best derived from the following syntheses of anthracene and its simple derivatives.

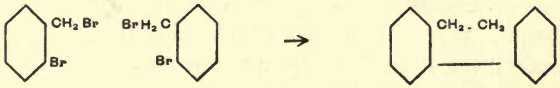
(1) By heating benzyl chloride with aluminium chloride dihydroanthracene is obtained:




(2) Dihydroanthracene is also formed by treating an ethereal solution of *o*-**brombenzyl bromide** with sodium:

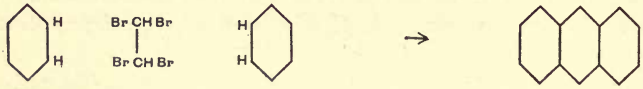



At the same time the molecules are condensed in a different way, **dihydrophenanthrene** being obtained:

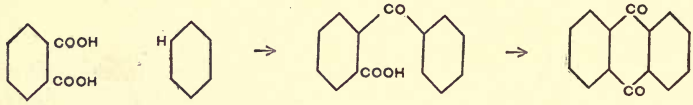



(3) By distillation of *o*-**tolylphenylketone** with zinc dust:

(4) By the Friedel and Crafts' reaction from benzene and acetylene tetrabromide:



(5) By distilling *o*-benzoylbenzoic acid with phosphoric anhydride:



*o*-Benzoylbenzoic acid Anthraquinone

**Estimation of Anthracene.**—The determination of the amount of anthracene in the commercial product is of considerable technical importance. The method in general use was devised by **Luck** and depends on the oxidation of the crude material and isolation and quantitative estimation of the anthraquinone produced.

The crude anthracene is dissolved in boiling glacial acetic acid and an acetic acid solution of chromic acid slowly added until the yellow colour persists on further boiling. The solution is then poured into water and the precipitated crude **anthraquinone** is collected and dried. To purify this it is heated on the water-bath with twice its weight of concentrated sulphuric acid. On pouring into water pure anthraquinone is precipitated, the impurities remaining in solution as sulphonic acids. The anthraquinone is then collected, dried and weighed.

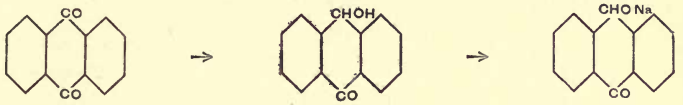
**Anthraquinone** is one of the most important derivatives of anthracene, particularly from a commercial standpoint, since its preparation forms the first step in the manufacture of alizarin.

In the laboratory it is prepared by oxidising anthracene with an acetic acid solution of chromic acid and subliming the product. Commercially the oxidation is carried out by a mixture of sodium dichromate and sulphuric acid. The anthracene, however, must be very finely divided to react with this mixture, and is thus prepared by distilling it in a current of superheated steam and

suddenly cooling the vapours with a jet of cold water. If necessary the anthraquinone may be purified by digestion with warm concentrated sulphuric acid as described above.

Anthraquinone sublimes readily, as forming pale yellow needles melting at 275°. It is insoluble in water and sparingly soluble in most organic solvents. It dissolves readily in glacial acetic acid and in benzene.

The most characteristic reaction of anthraquinone is its reduction to **oxanthranol,** which dissolves in caustic soda, forming a red sodium compound. The test is carried out by heating anthraquinone with zinc dust and caustic soda, when the red coloration is produced:




Anthraquinone Oxanthranol Red sodium compound

On exposure to air the colour disappears, owing to oxidation.

Anthraquinone is reduced to anthracene on distillation with zinc dust.

Anthraquinone, like α-naphthoquinone, is probably a **diketone** rather than a true quinone since it is only slightly coloured, is odourless and is not reduced by sulphurous acid. Moreover, the CO group is reduced to CHOH and not to C(OH) as in the case of a quinone.

**Alizarin,** $C_{14}H_8O_4$, 1.2 dioxyanthraquinone, is one of the most important of the synthetic dyestuffs. It occurs in *madder* (from which source it had been prepared for many years previous to its synthetical production) as the glucoside **ruberythric acid,** which breaks down under the action of the accompanying enzyme into glucose and alizarin.

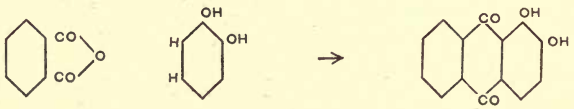
The first step in the discovery of the constitution of alizarin was made by Graebe and Liebermann (1868), who found that on distillation with zinc dust **anthracene** was obtained. They also showed that alizarin is soluble in caustic alkalis and gives a diacetyl derivative and therefore possesses the formula $C_{14}H_6O_2(OH)_2$, *i.e.* is probably a **dioxyanthraquinone.** They

therefore attempted to synthesise it by brominating anthraquinone and fusing the dibromo compound with potash. By a fortunate coincidence, of the **ten possible dibromoanthraquinones** the 1.2 compound was obtained and on fusion with potash this yielded alizarin.

This process, involving the use of bromine, was too expensive to become of technical importance, but in 1870 the method at present in use was patented almost simultaneously by **Perkin** in England and by **Graebe and Liebermann** in Germany. Anthraquinone on heating to 170° with fuming sulphuric acid yields a $\beta$-sulphonic acid. The sodium salt of this acid on fusion with caustic soda and the theoretical amount of potassium chlorate yields the disodium salt of alizarin :

The melt is extracted with water and mixed with milk of lime which precipitates the alizarin as the insoluble calcium salt. This on treatment with acid deposits alizarin as a yellowish-brown amorphous powder which may be collected and dried but is usually put on the market as a 20 per cent. paste with water.

The accepted constitution of alizarin has been conclusively proved by the synthesis from phthalic anhydride and catechol, which condense under the influence of hot concentrated sulphuric acid, yielding alizarin :




This condensation might be equally well represented by the formation of a 2.3 dioxyanthraquinone, but this alternative is discounted by the fact that alizarin yields two nitro derivatives with the nitro groups in the same ring as the hydroxyl groups, whereas a 2.3 dioxyanthraquinone could only give one such nitro compound.

Alizarin in the amorphous form is a yellow solid insoluble in water and melting at 290°. It may be sublimed, when it forms beautiful scarlet needles.

It dissolves readily in caustic soda, yielding a purple solution of **sodium alizarate.** If this solution is mixed with salts of many of the heavy metals the corresponding alizarates are precipitated.

These insoluble compounds are known as **lakes** and are largely used as pigments.

The colour of the lake varies with the metallic hydroxide used, and therefore a range of colours all derived from alizarin may be developed on a fabric by mordanting this with designs stamped on the cloth with different mordants thickened with gum. The following are some of the chief lakes of alizarin:

| | |
|---|---|
| Calcium | blue-purple |
| Strontium | red-purple |
| Barium | purple |
| Magnesium | violet |
| Copper | brown-violet |
| Mercury | black |
| Aluminium | red |
| Chromium | brown |
| Iron (ferrous) | black-violet |
| ,, (ferric) | brown-black |
| Tin (stannous) | red-purple |
| ,, (stannic) | blue-purple |

The calcium, barium, chromium, iron and tin lakes are the only ones of particular commercial importance.

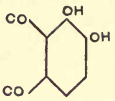
Alizarin is applied to cotton in the form of these lakes. The fabric is "mordanted" by impregnating it with the acetate of the desired metal and then exposing to steam. The acetate is hydrolysed and the acetic acid volatilises, leaving the metallic hydroxide.

On passing the prepared fabric through a bath of finely divided alizarin the insoluble coloured lake is deposited in the fibre.

If the mordant (thickened with glue) is applied to the cloth in a pattern, this pattern is, of course, finally produced in colour.

**Purpurin**, 1.2.4 trioxyanthraquinone, is prepared by oxidis-

ing alizarin with manganese dioxide and sulphuric acid. It occurs in madder and closely resembles alizarin in properties.

Several other oxyanthraquinones are known, some of which are used as dyestuffs, but according to **Kostanecki** only those containing the grouping  will form lakes and therefore be of any practical use.

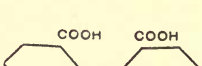
**Phenanthrene**, $C_{14}H_{10}$, accompanies anthracene to a considerable extent in the "anthracene oil" and is partially separated from this hydrocarbon by extraction with various solvents, as it is more soluble than anthracene.

Phenanthrene crystallises in colourless plates melting at 99° and boiling at 340°. Its **picrate** forms yellow needles melting at 145°. The constitution is deduced from the following syntheses:

(1) By passing the vapour of *o*-**ditolyl** through a red-hot tube:

$$\begin{array}{l} C_6H_4 \cdot CH_3 \\ | \\ C_6H_4 \cdot CH_3 \end{array} = \begin{array}{l} C_6H_4 - CH \\ | \quad \| \\ C_6H_4 - CH \end{array} + 2\,H_2$$

(2) Together with dihydroanthracene by the action of sodium on *o*-**brombenzyl bromide** (p. 119).

On oxidation phenanthrene yields **diphenic acid**: 

Phenanthrene is oxidised by an acetic acid solution of chromic acid to **phenanthraquinone.**

**Phenanthraquinone,** , crystallises in orange needles melting at 201°, and seems in some respects to resemble a quinone and in others a diketone such as anthraquinone. Thus, on the one hand, it is highly coloured and is reduced by sulphurous acid to the corresponding quinol, while on the other

hand it is odourless, non-volatile in steam and forms a bisulphite compound.

It may be used in the place of isatin (p. 15) as a very delicate test for thiophene, which produces a bluish-green coloration with phenanthraquinone dissolved in acetic and sulphuric acids.

## CHAPTER XVIII

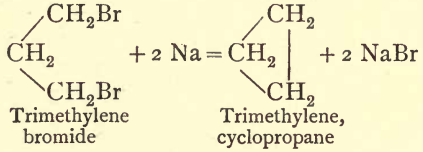
## THE POLYMETHYLENES

THESE hydrocarbons (also known as the **cycloparaffins**) are ring compounds of the general formula $(CH_2)_n$ and are therefore isomeric with the open-chain olefines. The two classes are, however, entirely different in chemical nature, the ring compounds being much more stable towards reagents.

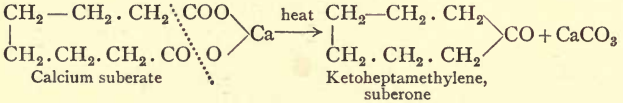
Before describing these compounds in detail it will be advisable to mention a few of the general reactions by which they (or their simple derivatives) may be prepared.

### General Methods of Preparation

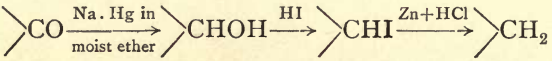
(1) By heating a dihalogen compound with sodium :



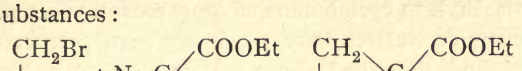

(2) By distillation of the calcium salt of a dibasic acid a cyclic ketone results :



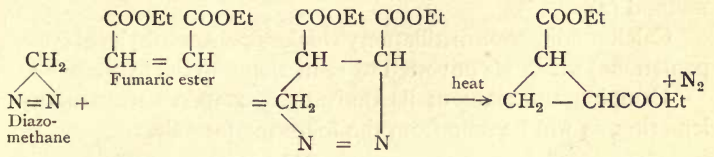

The ketone may be converted into the cycloparaffin by the following reactions :



(3) By the interaction of dihalogen compounds and the sodio-derivatives of malonic ester, ethane-tetracarboxylic acid or similar substances:

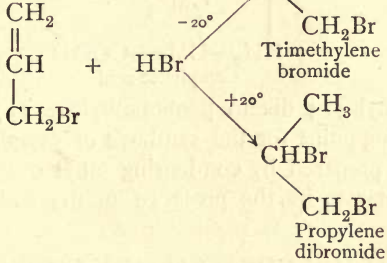


(4) By the action of diazo methane on fumaric ester or similar compounds a pyrazole-derivative is formed which on distillation loses nitrogen, yielding a carbocyclic compound:




Several other methods are available for the preparation of particular members of this series.

**Trimethylene**, cyclopropane, is prepared from trimethylene bromide and sodium. (Trimethylene bromide is obtained by the addition of allyl bromide and hydrobromic acid at −20°. At ordinary temperatures propylene dibromide is formed.)




The carboxylic acids are prepared by methods (3) or (4).

Trimethylene is a gas liquefying at −35°. It reacts with halogens and halogen acids, with rupture of the ring and production of trimethylene halides and alkyl halides respectively. It

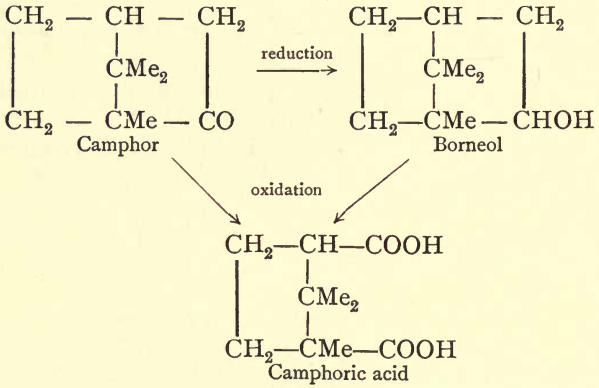
is more stable than its olefinic isomer propylene, being practically unattacked by dilute potassium permanganate.

**Tetramethylene**, cyclobutane, has only recently been prepared, though many derivatives have previously been prepared by the general methods described above. It is a gas at ordinary temperatures condensing at 12°. It is much more stable towards reagents than cyclopropane, being unattacked by bromine water and by cold halogen acids.

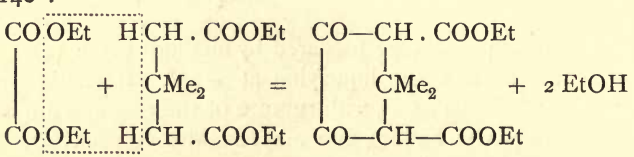
**Pentamethylene**, cyclopentane, was first prepared by method (2).

Calcium adipate on distillation yields ketopentamethylene (cyclopentanone) which is converted by reduction into the hydrocarbon.

Camphor and many of its derivatives contain a pentamethylene ring, as will be seen from the following formulæ:




1.1 Dimethyl 3.4 diketo pentamethylene 2.5 dicarboxylic ester, the starting-point for the synthesis of camphoric acid and of camphor, is prepared by condensing ethyl oxalate with ethyl $\beta\beta$-dimethylglutarate in the presence of dry sodium ethoxide at 140°:



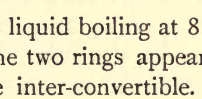
Pentamethylene is a volatile liquid (b.p. 51°) and it occurs to a considerable extent, mixed with other polymethylenes, in Russian petroleum. It is the most stable member of this series, being unattacked by boiling halogen acids.

**Hexamethylene**, cyclohexane, hexahydrobenzene, is the most important of the cycloparaffins, being the parent hydrocarbon of the hydro-aromatic compounds. These derivatives of hexamethylene are formed when aromatic compounds are reduced either by heating under pressure with hydriodic acid, or, better, by the **Sabatier and Senderens** method. This consists in bubbling hydrogen through the nearly boiling aromatic compound and passing the resulting gaseous mixture through a tube filled with **reduced nickel** powder at 200°. Under these conditions benzene yields cyclohexane, phenol cyclohexanol, aniline cyclohexylamine, etc.

Hexamethylene is a liquid boiling at 81° and like pentamethylene is very stable. The two rings appear to be of almost equal stability since they are inter-convertible. Thus hexamethylene when heated with aluminium chloride yields methylpentamethylene while camphoric acid under similar conditions yield a hexamethylene derivative.

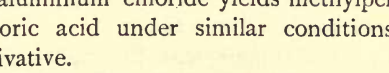
**Heptamethylene** is best prepared by the reduction of suberone, the distillation product of calcium suberate. It boils at 119° and is less stable than penta- or hexamethylene. On heating with hydriodic acid to 250° it yields methylhexamethylene and then dimethylpentamethylene.

**Octamethylene** has been prepared by Willstätter by a complex series of reactions from the alkaloid **pseudo-pelletierine**:



It is less stable than heptamethylene.

**Nonomethylene** has been prepared by method (2) by distilling calcium sebacate:



It is an unstable substance. No higher member of the series has yet been prepared. The polymethylenes appear to form a distinct class of compounds having the properties neither of the paraffins or the olefines. In reactivity they appear to be **intermediate between the unsaturated olefine and the saturated paraffin.** In each case, comparing olefine, cycloparaffin and paraffin of equal carbon content, the boiling-point of the cycloparaffin is the highest and the molecular volume the lowest of the three.

Among the cycloparaffins themselves it will be noticed that the **stability of the ring increases up to pentamethylene** and then **decreases again.**

**Baeyer** in 1885 explained this fact by his "**Strain Theory**" which he developed along the following lines:

The valencies of a carbon atom according to the modern theory lie along the lines joining the centre of a regular tetrahedron to the angular points, the carbon atom being supposed at the centre of this tetrahedron. Normally (*i.e.* when there is no internal distortion) the lines indicating the valencies make with each other an angle of **109° 28′.**

In the case of trimethylene the carbon atoms presumably lie at the angular points of an equilateral triangle (since trimethylene is symmetrically constituted) and the valencies joining the carbon atoms therefore make with each other an **angle of 60°.** As in the original unstrained condition the valencies lie at an angle of 109° 28′ the two bonds uniting the carbon atoms have together been diverted through an angle of 109° 28′ − 60° (or 49° 28′), **each valency therefore being diverted through an angle of 24° 44′.** Following the same line of reasoning the angle of distortion of each valency joining carbon atoms is as follows:—

| | | |
|---|---|---|
| Ethylene | ½ (109° 28′ − 0°) | = 54° 44′ |
| Trimethylene | ½ (109° 28′ − 60°) | = 24° 44′ |
| Tetramethylene | ½ (109° 28′ − 90°) | = 9 °44′ |
| **Pentamethylene** | ½ (109° 28′ − 108°) | = 0° 44′ |
| Hexamethylene | ½ (109° 28′ − 120°) | = − 5° 16′ |
| Heptamethylene | ½ (109° 28′ − 128° 34′) | = − 9° 33′ |
| Octomethylene | ½ (109° 28′ − 135°) | = − 12° 46′ |
| Nonomethylene | ½ (109° 28′ − 140°) | = − 15° 16′ |

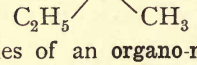
We see, therefore, that as the series is ascended the internal strain due to the distortion of the valencies from their normal position decreases to the very slight value in the 5 carbon chain and then increases in the opposite direction. We may fairly assume that the ease with which the ring is broken depends on the internal strain and these figures agree very remarkably with the known stability of the polymethylenes, which increases up to pentamethylene and then falls again, hexamethylene being almost as stable as pentamethylene while nonomethylene is quite unstable.

## CHAPTER XIX

### THE GRIGNARD REACTION

IT will be remembered that zinc dissolves in alkyl iodides, yielding compounds of the type $Zn(CH_3)_2$, which are highly reactive and have been of great value in synthetic chemistry. The chief disadvantage lies in the difficulties of manipulation since the zinc alkyls are spontaneously inflammable liquids.

In 1899, **Grignard**, at the suggestion of Professor **Barbier** (of the Sorbonne), undertook an investigation of the action between magnesium and the alkyl halides, since Barbier had found a mixture of magnesium and methyl iodide to react in a similar way to zinc methyl.

Grignard found that clean magnesium dissolves readily in an ethereal solution of an alkyl or aryl halide, giving a colourless solution. On evaporation a white solid is obtained which (taking methyl iodide as a typical halide) possesses the formula $CH_3MgI \cdot (C_2H_5)_2O$. The ether is persistently retained, even at 100°, and is probably combined as an **oxonium compound** of the formula  The solid possesses the characteristic properties of an **organo-metallic compound** reacting vigorously with moisture, carbon dioxide and with many organic compounds, the final products in each case being the same as those formed from zinc methyl. The magnesium methyl iodide (or **Grignard reagent** as the substance is frequently styled) possesses a great advantage over zinc methyl in that it is not inflammable.

The presence of ether, or at least of some substance which can combine with the magnesium compound, seems to be almost

a necessity. Magnesium will react with methyl iodide in benzene solution but only with difficulty and at a much higher temperature. If **ether, anisole** or **dimethylaniline** are added to the solution the magnesium immediately dissolves readily.

For practical use the Grignard reagent is prepared in the following way, great care being taken to ensure the **absence of, even traces of, water.** All the glass apparatus should be dried in the steam oven, and the liquids by distillation over some dehydrating agent (preferably phosphoric anhydride).

The alkyl or aryl halide is mixed with five times its volume of pure ether in a flask connected with a reflux condenser which is closed by a calcium chloride tube. To this solution is added the theoretical amount of magnesium ribbon, which has been cleaned with sandpaper to remove the surface film of oxide, and the whole is warmed on the water-bath. If no action commences after a few minutes a trace of iodine is added. This apparently has some effect on the surface of the magnesium, rendering it more susceptible to attack by the halide. When nearly all the metal has dissolved the reagent is rapidly poured into a dry ethereal solution of the substance with which it is to react. The reaction is usually vigorous and the white magnesium addition compound separates out. The mixture is then heated for half an hour and poured on to a mixture of crushed ice and dilute hydrochloric acid or ammonium chloride. The hydrolysed product is then collected and purified by suitable means.

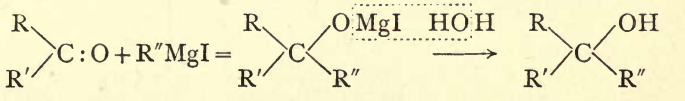
### Chief Reactions of the Grignard Reagent

(1) **With hydroxylic compounds** hydrocarbons are produced $CH_3MgI + ROH = CH_4 + Mg(OR)I$, where R may be hydrogen or any organic radical.

(2) **With halogen compounds** hydrocarbons are produced:

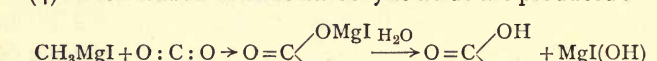
$$CH_3MgI + RCl = CH_3 . R + MgICl.$$

(3) **With aldehydes and ketones** alcohols are produced:

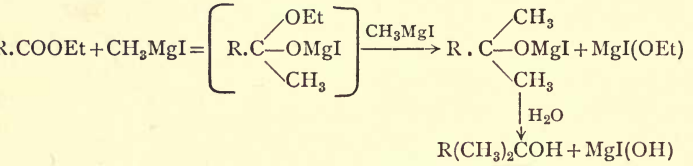


Formaldehyde (in the form of trioxymethylene) therefore gives primary alcohols, other aldehydes secondary alcohols and ketones tertiary alcohols.

(4) **With carbon dioxide** carboxylic acids are produced:

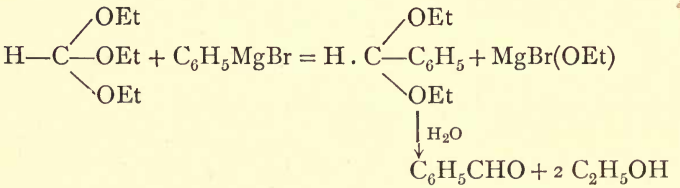


(5) **With esters** various products are obtained, depending on the particular esters and the proportions used. The CO group is the usual point of attack.



(*a*) With a formic ester a secondary alcohol is formed. With acetic and higher esters tertiary alcohols result.

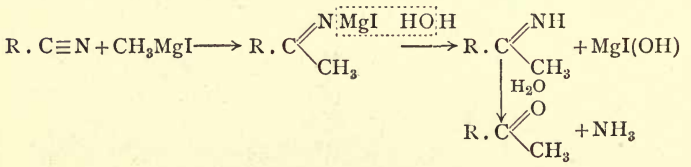
(*b*) Ethyl orthoformate yields aldehyde. Benzaldehyde has been prepared as follows:



(*c*) Ethyl chloro-carbonate is converted into ethyl acetate:

$$ClCOOEt + CH_3MgI = CH_3COOEt + MgICl$$

(6) **With nitriles** ketones are produced:



With cyanogen the reaction takes the following course:

$$NC.CN + CH_3MgI = NC.C(=NMgI)CH_3$$

$$NC.C(=NMgI)CH_3 + CH_3MgI = CH_3.C(=NMgI)CH_3 + MgI(CN)$$

$$CH_3.C(=NMgI)CH_3 + 2\,H_2O = CH_3.C(=O)CH_3 + NH_3 + MgI(OH)$$

(7) **With alkyl nitrites** hydroxylamine derivatives result:

$$O:N.OC_2H_5 + 2\,C_2H_5MgI = (C_2H_5)_2N.OMgI + MgI(OC_2H_5)$$

$$(C_2H_5)_2N.OMgI + H_2O = (C_2H_5)_2NOH + MgI(OH)$$

One of the many advantages of the Grignard reagent is the ease with which different products may be obtained at will from one starting material according as one, two, three or more molecular proportions of the magnesium compound is used. Thus from ethyl orthoformate an aldehyde, a secondary alcohol and a hydrocarbon may be successively prepared.

## CHAPTER XX

### STERIC (or SPATIAL) HINDRANCE

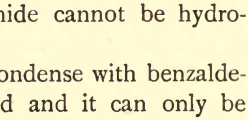
UNDER this term are correlated a large number of irregularities which have been met with from time to time in the progress of certain reactions.

From a few examples given below the derivation of the term, which expresses the influence of the **spatial propinquity** of neighbouring atoms on the reactivity of an atom or radical, will be evident.

(1) In 1872, **Hofmann** found that the $NH_2$ group in pentamethyl aminobenzene, $C_6(CH_3)_5 . NH_2$, could not be methylated with methyl iodide, and he suggested that this non-reactivity was due to the proximity of the methyl groups to the nitrogen atom. This was the first noticed example of steric hindrance.

(2) Derivatives of benzonitrile, benzamide and benzoyl chloride in which there are **two substituents ortho** to the CN, $CONH_2$ or COCl groups only hydrolyse with considerable difficulty, while pentamethylbenzamide cannot be hydrolysed.

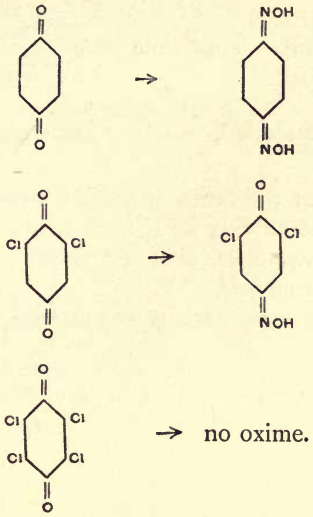
(3) 2.4.6 Tribromaniline will not condense with benzaldehyde to form the benzylidene compound and it can only be diazotised by using concentrated sulphuric acid and solid sodium nitrite. Dibromoaminoazobenzene,




where the *p*-bromine atom is replaced by the larger *benzene azo* group, cannot be diazotised even under these conditions.

(4) Kehrmann has shown that whereas quinone forms a

dioxime, dichloroquinone will only form a monoxime and **chloranil yields no oxime.**

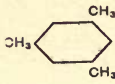
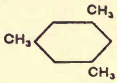



(5) The reactivity of ketones towards sodium bisulphite and hydrocyanic acid rapidly diminishes as the alkyl group increase in size. Thus acetone reacts readily and methyl ethyl ketone much more slowly, while diethyl ketone does not form a bisulphite compound.

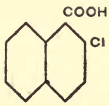
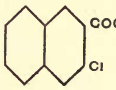
(6) A large amount of work on this subject has been carried out by **V. Meyer, Sudborough** and their co-workers, in connection with the rate of esterification of substituted acids. The method consisted in dissolving the acid in excess of alcohol containing 3 per cent. of hydrogen chloride (the **Fischer-Speier** method) and measuring the amount of ester produced after definite intervals. The following results may be mentioned :

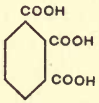
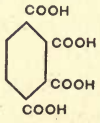
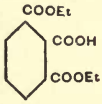
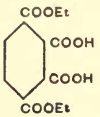
(*a*) Ortho-substituted benzoic acids esterify more slowly than the *m* and *p* isomers.

(*b*) Diortho-substituted benzoic acids esterify very slowly, though if one ortho position is unsubstituted esterification proceeds without difficulty.

(*c*) If the carboxyl group is removed from the proximity of these ortho substituents esterification proceeds readily. Thus while  cannot readily be esterified,  esterifies readily.

Even the ortho hydrogen atoms or possibly the benzene ring itself have a hindering effect, since phenylacetic acid esterifies more readily than benzoic acid.

(*d*) An adjoining nucleus may exercise the same influence as an ortho substituent. Thus whereas  esterifies very slowly,  reacts quite readily.

(*e*) Hemimellitic acid,  , and prehnitic acid,  , yield  and  respectively, while mellitic acid, $C_6(COOH)_6$, forms no ester.

(*f*) Substituted acetic acids esterify more slowly the larger the volumes and the greater the number of the substituting groups. Tribromacetic acid esterifies three hundred times more slowly than acetic acid.

It has been shown conversely that the esters which are difficult to prepare are also difficult to hydrolyse when once they are obtained, owing, no doubt, to the difficulty experienced by the molecules of the water of hydrolysis in reaching the ester grouping.

The above-mentioned cases of steric hindrance are typical, and similar examples are constantly being met with in ordinary laboratory work.

# APPENDIX I

## IMPORTANT SYNTHETICAL REACTIONS, ETC.

AS many reactions and discoveries described in the text are usually referred to by the name of the discoverer, the following summary of these may prove useful:—

**Armstrong and Baeyer** (p. 6) proposed the centric formula for benzene.

**Baeyer's Strain Theory** (p. 130).—The relation between the stability and internal strain of ring systems.

**Cannizzaro Reaction** (p. 78).—The auto-oxidation and reduction of an aromatic aldehyde under the influence of concentrated potassium hydroxide:

$$2\,C_6H_5CHO + KOH = C_6H_5CH_2OH + C_6H_5COOK$$

**Claisen Reaction** (p. 81).—The formation of an unsaturated aldehyde by condensing an aromatic aldehyde with an aliphatic aldehyde or ketone in the presence of dilute caustic alkali:

$$C_6H_5CHO + CH_3CHO = C_6H_5CH:CH.CHO + H_2O$$
$$C_6H_5CHO + CH_3COCH_3 = C_6H_5CH:CH.COCH_3 + H_2O$$

**Crum Brown and Gibson's Rule** (p. 10).—For determining the position a new substituent will take up when entering a substituted benzene ring.

"If the substituent group already present is X and if HX can be directly oxidised to HOX, any new substituent will go *meta* to X; If not, *ortho* or *para* (usually both)."

**Etard Reaction** (p. 80).—The oxidation of the side-chain methyl group of a hydrocarbon to the aldehyde group by mixing

with chromyl chloride in carbon disulphide solution and pouring on to ice:

$$C_6H_5 . CH_3 + 2\ CrO_2Cl_2 + H_2O = C_6H_5CHO + Cr_2O_3 + 4\ HCl$$

**Fischer-Speier Method.**—Esterification of an acid by warming with excess of the alcohol containing 3 per cent. dry HCl gas or sulphuric acid.

**Fittig Reaction** (p. 17).—The preparation of hydrocarbons by treatment of two halogen compounds with sodium in ethereal suspension:

$$C_6H_5Br + CH_3I + 2\ Na = C_6H_5CH_3 + NaI + NaBr$$

**Friedel-Crafts' Reaction** (p. 17).—The condensation of an aromatic substance (usually a hydrocarbon) with an aliphatic halogen compound by means of anhydrous aluminium chloride in carbon disulphide suspension:

$$C_6H_6 + C_2H_5Cl = C_6H_5C_2H_5 + HCl$$
$$C_6H_6 + CH_3COCl = C_6H_5COCH_3 + HCl$$

**Gattermann Reaction** (p. 59).—The elimination of nitrogen from a diazonium salt in the cold by the addition of finely divided copper (from copper sulphate and zinc dust):

$$C_6H_5N_2X = C_6H_5X + N_2$$

**Kekulé** (p. 6).—Proposed the six membered ring formula for benzene.

**Kolbe Reaction** (p. 92).—The preparation of phenolic acids (particularly salicylic acid) by heating the sodium salts of phenols in a current of carbon dioxide. At low temperatures (about 130–150°) *o* acids are obtained, while at 200° the para compounds predominate:

$$C_6H_5ONa + CO_2 = C_6H_5OCOONa$$
$$C_6H_5OCOONa = C_6H_4(OH)COONa$$

**Körner's Absolute Principle of Orientation** (p. 9).—To determine whether a di-derivative is an ortho, meta or para compound, introduce one more substituent group and find how many isomers are produced. Ortho compound give two, meta three, and para one tri-derivative.

**Liebermann's Reaction** (p. 68) for phenols or nitroso com-

pounds. If to a dilute solution of a nitroso compound in warm concentrated sulphuric acid a phenol is added, a blue colour is developed which turns red on dilution with water and blue again on making alkaline. The test is not applicable to all phenols.

**Perkin Reaction** (p. 90). — The condensation of aromatic aldehydes with the sodium salts of aliphatic acids in boiling acetic anhydride solution, with the production of unsaturated acids:

$$C_6H_5CHO + CH_3COONa = C_6H_5CH : CH . COONa + H_2O$$

**Reimer Reaction** (p. 82).—The condensation of phenols in hot alkaline solution with chloroform or carbon tetrachloride with the formation of oxyaldehydes or oxyacids. A mixture of ortho and para isomerides is produced.

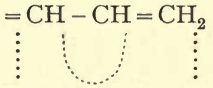
**Sabatier and Senderens** (p. 129).—Reduction of unsaturated compounds (particularly aromatic rings) to the saturated compound by passing the vapour of the substance mixed with hydrogen over heated nickel powder.

**Sandmeyer Reaction** (p. 58).—The elimination of nitrogen from a diazonium salt by adding this to a hot solution of a cuprous salt:

$$2\,C_6H_5N_2Cl + Cu_2X_2 = 2\,C_6H_5X + Cu_2Cl_2 + 2\,N_2$$

**Schotten-Baumann Reaction** (p. 69). — The benzoylation of an alcohol, phenol or amine by shaking in cold alkaline solution with a slight excess of benzoyl chloride until the odour of the latter has disappeared.

**Thiele's Theory of Conjugate Linkages** (p. 7).—Explanation of anomalous addition reactions of unsaturated compounds with conjugate linkages by assuming the unsaturated carbon atoms to possess a residual valency, two of which valencies may couple together when attached to adjacent carbon atoms; *e.g.*



**Zeisel Reaction** (p. 70). — The quantitative hydrolysis of methyl and ethyl ethers by boiling hydriodic acid:

$$ROCH_3 + HI = ROH + CH_3I$$

# APPENDIX II

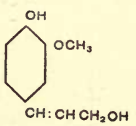
## THE CHIEF GLUCOSIDES

THE glucosides are naturally occurring vegetable compounds of unknown constitution, which on hydrolysis with dilute acid break down to a sugar (usually glucose) and some other compound. They are nearly always accompanied by an **enzyme** or ferment which will hydrolyse them under suitable conditions. They are anhydro compounds derived from the condensation of glucose with the other constituent with loss of water. Synthetic methyl glucosides have been prepared by the condensation of methyl alcohol and glucose in the presence of hydrochloric acid.

**Amygdalin** (p. 80) occurs in bitter almonds and in the kernels of many fruits. The accompanying enzyme in bitter almonds is **emulsin.** Amygdalin forms colourless soluble crystals melting at 200°. On hydrolysis with dilute acid or with emulsin it yields benzaldehyde, hydrocyanic acid and glucose. With concentrated hydrochloric acid it yields *l*-mandelic acid and glucose.

**Arbutin** occurs in the leaves of the bear-berry. On hydrolysis it forms glucose and quinol.

**Coniferin** occurs in the *Coniferæ* and on hydrolysis yields glucose and coniferyl alcohol,



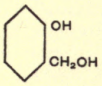

**Phloridzin** occurs in the bark of many fruit trees. On hydrolysis it yields glucose, phloroglucinol and phloretic acid.

**Potassium myronate** is present in mustard seed together

with its enzyme **myrosin**. On hydrolysis it yields glucose, potassium hydrogen sulphate and allyl mustard oil.

**Ruberythric acid** occurs in madder and on hydrolysis it breaks down into alizarin and glucose.

**Salicin** exists in willow bark and hydrolyses to saligenin,




, and glucose.

# APPENDIX III

## QUALITATIVE PRACTICAL ORGANIC CHEMISTRY

### Common Operations involved in Practical Organic Chemistry

**CRYSTALLISATION.**—An ideal solvent should dissolve a large amount of the solute when hot, but only a small amount when cold. It should not be very readily nor very difficultly volatile.

If the solvent to be used is not known, preliminary experiments must be made to find the one most suitable. A small amount of the substance is placed in a test tube and four drops of solvent added. If all dissolves the solvent is unsuitable. Otherwise the liquid is heated to boiling. If now only a small amount of substance dissolves the solvent is unsuitable. If a considerable amount dissolves the solution is decanted into another test tube, heated to boiling, cooled under the tap and rubbed with a glass rod. If crystals separate the operation may be repeated with the remainder of the substance. Even if the solvent is known a small trial experiment should be made to find approximately how much solvent is required. The following solvents should be tried in the order stated :—Water, alcohol, benzene, ligroin, glacial acetic acid, chloroform, pyridine, acetone.

If the substance is very soluble in one solvent and sparingly so in another a mixture of the two may give good results. The following table suggests the best solvent for various types of compounds :—

| Type | Solvent |
|---|---|
| Aromatic acids. | Water or benzene. |
| Higher fatty acids. | Ether. |
| Dibasic aliphatic acids. | Water or benzene. |
| Hydroxylic compounds. | Alcohol. |
| Acetyl compounds. | Water, alcohol or glacial acetic acid. |
| Nitro compounds. | Alcohol or nitrobenzene. |
| Osazones. | Alcohol. |
| Esters. | Alcohol or benzene. |
| Hydrocarbons. | Benzene. |
| Quaternary ammonium salts. | Aqueous alcohol. |

The substance to be crystallised should be powdered and boiled under reflux with rather less than the necessary amount of solvent, more of the latter being added from time to time as required. In the meantime a funnel (the stem of which has been cut off) is warmed and fitted with a plaited filter-paper cut to the correct size. The prepared solution is then poured on to the warm filter, the top of the funnel during the filtration being covered with a clock-glass and the filtrate received in a warmed beaker. (Crystallising dishes and evaporating basins are unsuitable.)

If the solute has a low melting-point the solution must be so diluted that the substance does not separate above its melting-point.

If solutions exhibit no signs of crystallising, scratching or seeding with a crystal of the substance is often effective.

When the solution is cold the crystals should be filtered (preferably at the pump), washed with a few drops of pure solvent and dried on porous tile. They should never be dried by application of heat, as this treatment of a moist substance generally produces fusion. If the solvent has a high boiling-point the crystals should be washed with a liquid of low boiling-point or the product may take some days to dry.

**Distillation.**—Almost all liquids and many solids are purified by distillation, either in steam or alone, at ordinary pressures or *in vacuo*.

An ordinary distillation is carried out by heating the substance in a distilling bulb attached to a Liebig condenser if the substance boils below 140° and to an air condenser if the

boiling-point is above 140°. A thermometer is fitted into the neck of the distilling bulb with the top of the mercury bulb slightly below the side tube to indicate the boiling-point. A small piece of porous pot should always be introduced to prevent bumping.

The first portion of the distillate usually consists of impurities. When the temperature is practically constant, the main fraction is collected in a clean dry vessel. When the temperature begins to rise again the distillation is stopped, the impurities of higher boiling-point remaining in the distilling flask.

If a highly purified product is required the process of fractional distillation is adopted. The separation is hastened by the use of a fractionating column. This consists of a long tube provided with obstructions which the vapours have to pass before reaching the condenser. During the course of this passage the vapour of the constituents of higher boiling-points condense to a considerable extent and flow back into the flask.

In carrying out a fractional distillation the liquid with a piece of porous pot is placed in the smallest suitable flask fitted with a column, thermometer and condenser, and distilled *slowly* to obtain efficient fractionation. A set of dry test tubes supported in a test-tube rack may be used as receivers.

Before distillation a liquid should always be dried or explosive boiling and loss of substance may result. Ethereal extracts must always be dried before distillation since ether dissolves 3 per cent. of water. If the amount of substance is so small that a considerable proportion would be absorbed by the drying agent it may be diluted with ether, the solution dried, and the ether subsequently distilled off on the water-bath. The desiccating agent used depends on the substance to be dried. Calcium chloride is generally employed, but cannot be used with alcohols or amines. These should be dried with potassium carbonate and caustic potash respectively. Unstable substances may be dried by anhydrous sodium sulphate.

### Determination of Melting-point

The melting-point of a solid organic substance is universally used as the criterion of purity. Before determining a melting-

point the substance should be thoroughly dried and rubbed to powder on a porous plate. It is next transferred to a capillary tube which is attached by capillary attraction to the thermometer so that the substance is opposite the middle of the mercury bulb. The capillary should not be attached to the thermometer by a rubber band. The melting-point bulb in which the thermometer and capillary are supported contains concentrated sulphuric acid and a small fragment of nitre to oxidise charred matter and so keep the acid clear.

The less pure the substance the lower and less definite is the melting-point. The final test, therefore, of the identity of two substances is the determination of the melting-point of a mixture of these substances. If they are identical the mixture will melt at the same temperature as the substances. Similarly a substance is known to be pure when further attempted purification (*e.g.* by crystallisation) does not raise the melting-point.

Since the mercury in the thermometer stem is not at the same temperature as that in the bulb the temperatures read off will be too low, the error increasing with increasing temperature.

This error may be corrected by arranging a second thermometer to indicate the mean temperature of the emergent mercury thread. Then $C = N(T - t) \times \cdot 000154$ where C = correction, N = number of degrees exposed, T° is the observed melting-point, t° the mean temperature of the emergent stem, and ·000154 is the apparent coefficient of expansion of mercury in glass. Unless otherwise stated melting-points are uncorrected.

**Determination of Boiling-point**

This may be done roughly by boiling 1 c.c. of the substance in a test tube and holding the thermometer bulb in the vapour away from the side of the tube.

A much more accurate method consists in distilling the substance from a small distilling bulb fitted with a thermometer. The side tube should dip into a test tube standing in a boiling tube or small beaker containing cold water. The boiling-point is read off when the temperature is steady (usually about half-

way through the distillation). The barometric pressure should be noted as the boiling-point changes about ·04° C. for each millimetre difference of pressure from 760 mm.

### Ether Extraction

The following points should be borne in mind when extracting a solution with ether :—

(1) Ether vapour is very heavy and inflammable.

(2) The tap and stopper should be held while shaking and the pressure released from time to time by opening the former.

(3) Several extractions with small amounts of ether are more effective than fewer extractions with larger quantities of ether.

(4) If the solution contains alcohol the extract should be shaken twice with water (if the substance extracted is insoluble in water) to remove alcohol.

(5) Ethereal extracts must be dried before distilling of the ether. Calcium chloride is generally used, but alcohols must be dried with potassium carbonate and amines with caustic potash.

**Acetylation.**—The substance (finely powdered if solid) is mixed with five parts of acetic anhydride and one part of fused sodium acetate and refluxed for two hours under an air condenser. Amines of simple constitution acetylate in a few minutes. The product is poured into dilute alcohol (15 per cent.) and warmed till all acetic anhydride has disappeared. On cooling and scratching the acetyl compound separates.

**Benzoylation** (Schotten-Baumann Method).—Suspend or dissolve the substance in dilute caustic soda, add *slightly* more than the theoretical amount of benzoyl chloride and shake in a corked flask until the smell of the benzoyl chloride has disappeared. Separate the benzoyl derivative by filtration or ether extraction.

**Hydrolysis.**—The choice of the hydrolysing agent depends on the substance and the nature of the products. For **esters**

30 per cent. caustic potash is most suitable. The mixture is refluxed (under a Liebig condenser) until the oily layer has disappeared or the odour of the ester has disappeared. (The former test will of course be valueless with isobutyl, amyl and benzyl esters.) The liquid is then distilled until one-third has passed over. The distillate is saturated with solid potassium carbonate when the **alcohol** separates and is collected, dried over potassium carbonate and redistilled.

Special tests must be applied to identify the nature of the acid before attempting to isolate it. If it is sparingly soluble in cold water (*e.g.* aromatic acids) it is isolated by acidifying and cooling the residue from the distillation. If volatile the liquid is nearly neutralised with sulphuric acid, evaporated to dryness and distilled with strong sulphuric acid. (This is impossible in the case of formic acid.) Other acids should be identified in the neutralised solution by colour or precipitation reactions.

Phenolic esters are best hydrolysed by equal volumes of sulphuric acid and water. Amides are readily hydrolysed by acids or alkalis. Nitriles are most quickly hydrolysed by dissolving in strong sulphuric acid, diluting and boiling. This preliminary treatment converts the nitrile into an amide.

Acyl derivatives of amines are best hydrolysed with strong hydrochloric acid. Alkali reacts very slowly.

### Preparation of Phenylhydrazones and Osazones

(*a*) *Phenylhydrazones.*—If the substance is a liquid it is mixed with an equal bulk of phenylhydrazine, when the reaction will proceed spontaneously. If a solid, it should be dissolved in warm alcohol or glacial acetic acid and phenylhydrazine, dissolved in the same solvent, added. The mixture is then boiled and allowed to cool, when the phenylhydrazone will crystallise out. It must be recrystallised before a melting-point is taken.

(*b*) *Osazones.*—The chief points to remember are :—

(1) The reaction takes some minutes and then only when the reagents are warm. The solution should be heated on the water-bath, *not boiled.*

(2) A considerable excess of water is necessary to precipitate the osazone. To prepare the osazone of a sugar 0·2 grm. is dissolved in 7 c.c. of water and mixed with a crystal of sodium acetate, five drops of phenylhydrazine and three drops of glacial acetic acid. On warming for ten minutes on the water-bath and, if necessary, diluting, yellow flocks of the osazone are deposited. The melting-point is not very characteristic as the osazones of the common sugars all melt at about 200° C. with decomposition.

### Preparation of Diazo and Azo Compounds

*To prepare a solution of a diazonium chloride.*

The amine is suspended or dissolved in $2\frac{1}{2}$ molecular proportions of hydrochloric acid diluted with four times its volume of water and crushed ice. Remember that *100 c.c. of concentrated hydrochloric acid contains about 36·5 grms. of hydrogen chloride.*

To the cold solution of the amine hydrochloride is now slowly added about 5 per cent. more than the theoretical amount of sodium nitrite (usually about 95 per cent. $NaNo_2$), dissolved in four times its weight of water. The reaction is exothermic, so ice should be added.

*To prepare an azo compound.*

If the second component is a phenol the theoretical amount is dissolved in dilute caustic soda solution, the weight of alkali being equal to the weight of hydrogen chloride employed for diazotisation. The diazo solution is then slowly poured (or filtered if it contains suspended solids) into the alkaline phenol solution. The coupling takes about three hours, after which the azo phenol is precipitated by neutralisation of the solution with acetic acid.

If the second component is an amine the theoretical amount is dissolved in glacial acetic acid and mixed with an equal bulk of water and crystallised sodium acetate, the weight of the latter being three times that of the hydrogen chloride employed. The

function of the sodium acetate is to remove the free hydrochloric acid which hinders coupling. The diazo solution is then added and after three hours the azoamine is filtered off.

### Identification of the Elements in an Organic Substance

A. **Metals.**—In many cases these may be detected by their ionic reactions, but frequently the metal exists as a complex anion and therefore cannot be detected by ordinary methods. In such a case it is necessary to destroy the organic matter present. This is carried out by one of the following methods :—

(1) By applying the usual dry tests, such as flame test, borax bead, etc.

(2) By igniting the substance on a crucible lid or a piece of platinum foil. The metal then remains as carbonate or oxide, or if sulphur is present, as sulphide or sulphate. The residue can then be analysed in the ordinary way. Special tests must of course be applied for mercury and ammonium.

B. **Carbon and Hydrogen.**—The presence of these elements is generally assumed. (Certain organic compounds, such as carbon tetrachloride, salts of oxalic acid, etc., contain no hydrogen.)

To test for the presence of carbon and hydrogen mix some of the well-dried substance in a test tube with freshly ignited copper oxide. Fit the test tube with a cork and delivery tube dipping into lime water and heat the mixture. The carbon is evolved as carbon dioxide and the hydrogen as water.

C. **Nitrogen.**—Fuse the substance in a bulb tube with a small piece of sodium, gradually raising the temperature to redness, and drop the tube gently into a test tube containing about 3 c.c. of distilled water. The bulb cracks, the excess of sodium dissolves and the sodium cyanide formed by the combination of sodium carbon and nitrogen is extracted from the carbonaceous residue by warming and filtering the solution. To a portion of the filtrate a few drops of ferrous sulphate solution are added, when ferrous hydroxide is precipitated and sodium cyanide con-

verted into ferrocyanide. On adding a drop of ferric chloride and acidifying, the presence of nitrogen is indicated by a bluish-green solution or a blue precipitate of ferric ferrocyanide. An indecisive coloration is made more distinct by filtration, the blue particles then showing clearly on the white filter paper.

$$\left.\begin{array}{l} 2\,NaCN + FeSO_4 = Fe(CN)_2 + Na_2SO_4 \\ 4\,NaCN + Fe(CN)_2 = Na_4FeC_6N_6 \end{array}\right\} \text{ in presence of alkali}$$

$$2\,Fe_2Cl_6 + 3\,Na_4FeC_6N_6 = Fe_4(FeC_6N_6)_3 + 12\,NaCl$$

D. **Sulphur.**—To a portion of the filtered solution from the sodium fusion add a few drops of sodium nitroprusside solution. A deep purple colour indicates sulphur. (The solutions must be *cold* and *alkaline* to give this test.) If the original substance contains both sulphur and nitrogen and an insufficiency of sodium is used, all the sodium will combine with the sulphur, and hence nitrogen may be missed. If, therefore, sulphur is found the nitrogen test should be repeated, using more sodium.

E. **Halogens.**—(1) Heat a copper wire in the bunsen flame till it ceases to colour the flame green. Allow it to cool, dip it into the substance and heat again. If a halogen is present a bright green flame is produced. (This test is useless in the presence of acids; *e.g.* urea nitrate and acetic acid would both give this test.)

(2) Acidify a portion of the filtrate from the sodium fusion with nitric acid, boil for a minute to expel hydrocyanic acid and add silver nitrate solution. A white or pale yellow precipitate indicates halogen. To identify the halogen slowly add ammonia. Silver chloride is readily soluble, silver bromide is less soluble and silver iodide is insoluble. Particular care must be taken with this test since silver cyanide and silver chloride are almost identical in physical and chemical properties. The copper wire test is on the whole more reliable, though it affords no evidence as to the particular halogen present.

F. **Phosphorus.**—Phosphorus compounds are rarely met with except as phosphates of bases and in certain proteins. The element is detected by fusing the substance with nitre and

sodium carbonate and testing the product for phosphate with ammonium molybdate.

### Identification of Simple Organic Substances

Since the majority of organic substances do not ionise in solution no definite scheme of analysis can be drawn up. The method adopted in organic chemistry consists in first of all determining the class of compound to which the substance belongs by means of some characteristic reaction of that class. Special tests (such as melting-points) are then applied to determine which member of the class is under investigation. Suppose, for example, the substance is acetamide. By testing with caustic soda we find that ammonia is evolved only on heating. The substance is therefore an amide. Since it melts at 82° it is probably acetamide. This is confirmed by testing the alkaline solution after hydrolysis for sodium acetate. Absolute proof may be supplied by a mixed melting-point determination.

**Preliminary Tests—**

(1) **Note colour, smell,** etc.

(2) **Heat a small amount** on a knife blade or platinum foil. Apply heat, gently at first and afterwards more strongly. If the substance burns with a smoky flame it is aromatic. If not, it is probably aliphatic. Note whether the substance melts, explodes, chars or leaves any residue. Explosion suggests nitro or nitroso compounds or nitrates of bases. Charring without fusion suggests sulphonic acids or metallic salts. Non-volatile residue indicates a metallic radicle, probably from a salt of an acid or a bisulphite compound. Identify the metal by ordinary analysis. Carefully note any odour evolved on heating.

(3) **Test for elements** (p. 153). These tests must be carried out very carefully and repeated if indecisive results are obtained, since the whole scheme of identification depends on a knowledge of the elements present. If a very pronounced nitrogen test is obtained, the presence of a CN group may be suspected. If

sodium produces effervescence in the cold, a hydroxylic substance is probably present. The odour of any vapours evolved during the ignition should be noted. Nitro compounds explode or produce thick black soot. Nitrates of bases explode.

(4) **Shake in a test tube with cold caustic soda.** Evolution of ammonia indicates an *ammonium* salt. A fishy ammoniacal smell indicates an aliphatic amine. Aromatic bases are liberated from their salts by this treatment. If the substance is insoluble in water but soluble in alkali it is acidic in nature.

(5) **Boil with caustic soda.** If ammonia develops only on boiling an amide, imide or nitrile is present. The residual solution should be investigated to identify the acid.

(6) **Add dilute hydrochloric acid.** If the substance is insoluble in water but soluble in acid it is probably a base.

(7) **Add cold concentrated sulphuric acid** and slowly raise the temperature to boiling-point. Note any charring and odour, inflammability, etc., of any gases evolved. Test for carbon monoxide and dioxide. Remember the boiling acid with organic matter evolves sulphur dioxide.

(8) **Add ferric chloride** to the **neutral** solution. If the solution is not neutral it must be *exactly* neutralised, using litmus paper and very dilute ammonia or nitric acid. The ferric chloride must be made neutral by adding ammonium hydrate.

A *red coloration* indicates formate, acetate, or, if very intense, a thiocyanate.

A *yellowish precipitate* indicates succinate, phthalate, benzoate, hippurate, cinnamate and certain other acid radicles.

A *purple coloration* indicates a monohydric phenol, resorcinol or *o* hydroxy acids. Certain substituted phenols (*e.g.* nitrophenols) give no colour. Catechol derivatives give a *blue or green* colour.

(9) **Warm with Fehling's solution.** Rapid reduction indicates an aldehyde, sugar or hydrazine. In the latter case nitrogen is evolved.

(10) **Taste** only if either *metal or nitrogen are absent* (hence preventing any accidents with cyanides). This test will at once indicate acids, sugars, etc. Remember salts of organic bases are hydrolysed by water to free acid.

(11) **Heat with soda lime.** Carboxylic acids lose $CO_2$. Smell the evolved gases.

(12) **Try to make phenyl hydrazone.** (See p. 151.)

(13) **Add ammoniacal silver nitrate** to neutral solution and warm. Black deposit or silver mirror indicates aldehyde, sugar or tartaric acid.

(14) **Add bromine water.** Most phenols and amines give a white precipitate.

Unsaturated compounds decolorise without precipitation.

If no action add sodium hypobromite. Effervescence indicates urea or ammonium salt.

(15) **Add Schiff's solution.** Red colour *in the cold* indicates an aliphatic aldehyde.

(16) **Add slightly ammoniacal calcium chloride.** White precipitate of oxalate and tartrate in cold, citrate on boiling.

(17) **Find the melting-point or boiling-point.** Always test whether the substance will melt before attempting a melting-point determination. Always thoroughly dry and powder the substance before determining a melting-point. A trace of water may depress the melting-point by 10° C. A derivative should whenever possible be recrystallised before a melting-point is taken.

The above tests will, as a rule, indicate the class to which the substance belongs. If the substance is *very non-reactive* it is probably a *hydrocarbon, ether or ester.*

In the first case identification depends on melting- or boiling-point. Certain aromatic hydrocarbons may be characterised by the melting-points of their **picrates.** These are prepared by mixing alcoholic or benzene solutions of the hydrocarbon and of picric acid and allowing the picrate to crystallise. The product should be washed with a little pure solvent before drying.

Certain ethers, particularly those derived from phenols, may be decomposed by refluxing for an hour with strong hydriodic acid. The reaction products may then be isolated and investigated.

If the substance is an ester (usually indicated by the odour)

it should be hydrolysed by caustic potash. If it will not yield to this treatment 50 per cent. sulphuric acid will probably prove effective.

If an aromatic primary amine or phenol is suspected it may be identified by the preparation of an azo dye. This is carried out by dissolving the amine in *cold* dilute hydrochloric acid, adding a little sodium nitrite and *pouring into* a cold caustic soda solution of $\beta$-naphthol, or, conversely, by diazotising some aniline and pouring into an alkaline solution of the suspected phenol. A red product indicates the formation of an azo compound.

The above tests will probably have suggested the nature of the compound.

The following tables of confirmatory tests deal separately with the two main classes, *aliphatic* and *aromatic*, and are arranged according to the elements present in the substance. Only the more common substances which the student is likely to meet with are described.

## ALIPHATIC SECTION

A. **Carbon and Hydrogen** (and possibly a **Metal**).

If the substance is soluble, oxygen is present. If a metal is present, it is probably as the salt of an acid.

(*a*) **Alcohols (Monohydric).**

*Primary.*—Methyl, ethyl, *iso*-butyl, *iso*-amyl and allyl alcohols.

Butyl and amyl alcohols have an unpleasant odour of fusel oil, while allyl alcohol has a pungent tear-exciting odour. All burn and all except butyl and amyl alcohols are miscible with water.

(1) *Add sodium.* Hydrogen is evolved and a white residue is left on evaporation.

(2) *Warm with acetic anhydride* and pour into warm water. Characteristic fruity odours of the acetates are produced.

(3) *Distil with potassium dichromate and dilute sulphuric acid* into water. Distillate smells of

aldehyde, turns Schiff's solution red and reduces ammoniacal silver nitrate. Allyl alcohol yields chiefly formic acid.

(4) *Add iodine solution to a little of the alcohol,* decolorise with caustic soda and warm. A smell of iodoform is produced with all except methyl and allyl alcohols.

Methyl alcohol is characterised by warming with salicylic and sulphuric acids, the methyl salicylate being detected by its odour (oil of wintergreen).

Allyl alcohol immediately decolorises bromine water and alkaline permanganate.

*Secondary and Tertiary.*—Expensive and uncommon.

**Trihydric.** The only important member is glycerol, a sweet viscous liquid which decomposes on heating, giving unpleasant-smelling vapours of acrolein. It reduces Fehling's solution on boiling. If a borax bead is moistened with glycerol and heated a green flame is obtained.

(*b*) **Aldehydes.**

*Formaldehyde* in aqueous solution ("formalin") has a pungent odour, reddens Schiff's solution, reduces Fehling's solution and blackens ammoniacal silver nitrate. Its insoluble tripolymer, paraformaldehyde, melts indefinitely at 170°, dissociating into formaldehyde. It is soluble in caustic soda.

*Acetaldehyde* is a volatile liquid (b.p. 21°) with a characteristic odour. It reddens Schiff's solution, reduces Fehling's solution and ammoniacal silver nitrate and with chromic acid mixture yields acetic acid. With boiling caustic soda it yields brown aldehyde resin. A drop of concentrated sulphuric acid converts aldehyde into an insoluble polymer, *paraldehyde* (b.p. 124°), which regenerates aldehyde on distillation with dilute acid.

(*c*) **Ketones.**—The only common ketones are acetone and methyl ethyl ketone. They possess a peculiar sweet

odour. They react with iodine and alkali (giving iodoform), with sodium bisulphite (giving a solid bisulphite compound) and with phenylhydrazine (giving liquid phenylhydrazones). They are distinguished by their boiling-points.

(*d*) **Acids.**—

**Monobasic.**

*Formic Acid.* Pungent-smelling liquid decomposed by warm $H_2SO_4$, giving carbon monoxide. The neutralised solution gives a red colour with ferric chloride and a brown precipitate on boiling. It reduces warm mercuric chloride solution to calomel.

*Acetic acid* possesses a smell of vinegar. It gives the same $FeCl_3$ reaction as formic acid. With alcohol and concentrated $H_2SO_4$ it gives a fruity odour of ethyl acetate.

*Palmitic and stearic acids* feel greasy and dissolve in alkalis, giving soap. They are reprecipitated on acidification and are distinguished by their melting-points.

*Lactic Acid.* Heavy syrup soluble in water. With warm $H_2SO_4$ it gives aldehyde and carbon monoxide and finally chars. Chromic acid mixture gives acetic and carbonic acids.

**Dibasic.**

*Oxalic Acid*, $2\,H_2O$. White crystals decomposed by hot strong $H_2SO_4$, giving carbon monoxide and dioxide. It reduces warm acid permanganate. Calcium chloride precipitates calcium oxalate (insoluble in acetic acid) from an alkaline solution.

*Succinic Acid.* White crystals decomposed on heating, evolving choking vapours of succinic anhydride. Neutral solution gives a buff precipitate with ferric chloride. On heating with twice its weight of resorcinol and a drop of strong sulphuric acid and extracting the melt with alkali a green fluorescence is obtained.

*Tartaric Acid.* Very soluble in water. Chars on heating, giving a smell of burnt sugar. Chars easily with hot

strong $H_2SO_4$ (cf. Citric acid). Reduces ammoniacal $AgNO_3$ on heating. The acid potassium salt is precipitated on shaking with potassium acetate and a drop of acetic acid. Calcium tartrate is insoluble in ammonia but soluble in acetic acid.

**Tribasic.**

*Citric Acid.* Chars on heating and evolves irritating vapours. Does not readily char with hot strong $H_2SO_4$. Calcium citrate is precipitated on boiling but not in the cold from an alkaline solution.

(*e*) **Esters.**—Usually pleasant-smelling liquids insoluble in water.

Methyl oxalate is solid and, like ethyl oxalate, has only a slight odour. Commercial methyl oxalate smells like acetamide. Methyl acetate and oxalate are soluble in water. Oxalic esters are readily hydrolysed even by hot water and with strong ammonia give white insoluble oxamide. Esters are identified by their boiling-points and products of hydrolysis (p. 151).

(*f*) **Carbohydrates.**

*Glucose.* Sweet, soluble solid which chars on heating. It chars with warm strong $H_2SO_4$, but least easily of all the carbohydrates. Boiling caustic soda turns it brown and gives a smell of burnt sugar on acidification. Glucose reduces Fehling's solution and ammoniacal $AgNO_3$ easily and gives an osazone (m.p. 204°).

*Lactose* is sparingly soluble in cold water and is only slightly sweet. It chars very easily with warm strong $H_2SO_4$, but otherwise resembles glucose.

*Cane Sugar* is the sweetest of all the sugars. It chars with cold strong $H_2SO_4$. It is not a reducing agent, gives no osazone and is unaffected by boiling NaOH. Boiling dilute acid gives glucose.

Sugars are best identified by their melting-points. Those of their osazones are too near each other to be of much value in identification.

*Starch.* Insoluble in cold water and gives starch paste

with boiling water. Coloured blue by iodine. Hydrolysed by boiling dilute acid to glucose.

B. **Carbon, Hydrogen and Halogen** (possibly **Metal**).

(If a metal is found, salts of haloid acetic acids are probably present.)

*Alkyl Halides.*—Heavy insoluble volatile liquids with a characteristic odour. Hydrolyse with caustic soda and identify the products.

*Chloroform and Bromoform.*—Heavy insoluble liquids with sweet odour. They give the characteristic odour of phenyl isocyanide with aniline and alkali (Carbylamine reaction). Only a trace of chloroform should be used. Boiling alcoholic potash gives KCl(KBr) and a formate.

*Iodoform.*—Yellow solid with characteristic odour and reactions like those of chloroform. Decomposed on heating, evolving iodine.

*Haloid Acetic Acids.*—Deliquescent solids ($CHCl_2COOH$ is liquid) smelling like acetic acid. $CHCl_2COOH$ with boiling potash yields oxalic and acetic acids. $CCl_3COOH$ under these conditions yields $CHCl_3$ and $CO_2$.

*Chloral hydrate* forms white soluble tables with a pungent odour. Cold strong $H_2SO_4$ gives an oily layer of chloral which unites eagerly with water. Chloral hydrate has none of the usual aldehyde reactions and with warm alkali gives chloroform and a formate.

C. **Carbon, Hydrogen, Nitrogen and Metal.**

**Cyanides** (except $Hg(CN)_2$) with warm dilute $H_2SO_4$ evolve HCN (recognised by odour). With concentrated acid the HCN is hydrolysed, evolving CO and leaving ammonium sulphate. Soluble cyanides give prussian blue when treated as in the test for nitrogen. Insoluble cyanides (except $Zn(CN)_2$) may be decomposed by boiling caustic soda and filtering off the metallic hydroxide. With $Zn(CN)_2$ the sodium zincate must be decom-

posed with ammonium chloride. Mercury cyanide on heating gives mercury and cyanogen, which burns with a lilac-pink flame.

*Ferrocyanides* are usually yellow or, when finely powdered, white. Those of the alkalis and alkaline earths are soluble. The silver, lead and zinc salts are white, the tin salt pale blue, the copper salt brown and the ferric salt dark blue. The last two afford characteristic tests for the $Fe(CN)_6'''$ ion. Ferrocyanides decompose like cyanides with hot strong $H_2SO_4$. On heating they blacken and decompose, giving $FeC_2$ and if moist evolve ammonia.

*Ferricyanides* are usually orange in colour. The ferrous salt is dark blue and is used as a test for the $Fe(CN)_6'''$ ion. Reducing agents convert ferricyanides into ferrocyanides.

### D. Carbon, Hydrogen and Nitrogen Present.

*Acetonitrile* is a volatile liquid, smelling like crude acetamide and hydrolysed by boiling acid to acetic acid and ammonia.

*Acetamide* is a white deliquescent solid, usually with a characteristic odour. It is readily hydrolysed.

*Oxamide* is a white insoluble infusible powder which yields ammonium oxalate on hydrolysis.

*Glycine* is a neutral solid the aqueous solution of which develops a fine blue colour with dilute copper sulphate solution. With nitrous acid it evolves nitrogen.

*Urea* (Carbamide) is a very soluble white solid crystallising in needles. On hydrolysis it yields ammonium carbonate. A strong solution yields a white precipitate of the nitrate with strong nitric acid. As an amide it reacts with nitrous acid, evolving nitrogen and giving the corresponding acid (in this case $H_2CO_3$). Nitrogen is also evolved with sodium hypobromite. When heated just above its melting-point for a minute it evolves ammonia and forms *biuret*. This is on extraction with water and treatment with **one drop** of copper sulphate solution and excess of caustic soda yields a purple coloration. The salts of urea are strongly acid in reaction and the nitrate is somewhat explosive.

**Amines.**—Volatile alkaline, inflammable, expensive liquids with an ammoniacal fishy odour. They give insoluble platinichlorides.

*Primary amines* react with nitrous acid, forming nitrogen and a primary alcohol.

*Secondary amines* with nitrous acid yield a yellow oily nitrosamine. Extract with ether, separate, wash and evaporate the ether solution, dissolve the nitrosamine in a little strong sulphuric acid. On adding a crystal of phenol a blue colour develops which turns red on dilution and blue again with alkali (Liebermann's nitroso reaction).

*Tertiary amines* do not react with nitrous acid but with alkyl halides yield solid soluble quaternary ammonium salts.

### E. Carbon, Hydrogen, Nitrogen and Halogen.

*Urea hydrochloride* is a deliquescent acid salt. The reactions with hypobromite and with nitrous acid are the same as those of urea.

*Salts of amines* are white soluble neutral salts resembling ammonium salts but are soluble in alcohol. Caustic soda liberates the free amine.

*Tetra-alkylammonium salts* resemble ammonium salts but are not decomposed by caustic soda. Distillation with lime gives the tertiary amine.

### F. Carbon, Hydrogen, Sulphur and Metal.

*Alkyl metallic sulphates* are soluble salts and only give a slight precipitate in the cold with barium chloride (due to traces of sulphates). Boiling dilute acid hydrolyses them to alcohol and metallic sulphate, which may be detected in the usual way. The dry salts on heating evolve ethylene and leave a metallic sulphate.

*Ketone bisulphite compounds* are soluble solids decomposed by acids or alkalis, regenerating the ketone.

G. **Carbon, Hydrogen, Nitrogen and Sulphur.**

*Metallic Thiocyanates*, if soluble, give a deep red colour with ferric chloride. Hot strong $H_2SO_4$ causes evolution of inflammable carbon oxysulphide.

## AROMATIC SECTION

Aromatic compounds are distinguished from the aliphatic compounds by the smoky flame with which they burn. Owing to the *ortho-*, *meta-*, *para*-isomerism a further complication is introduced. When the substituent groups have been identified, the relative positions are usually found by determining the melting-point or sometimes by considering the cost of the three isomers. Occasionally, as in the case of the dioxybenzenes, the reactions of the isomers are distinctive.

In this series we frequently have to deal with substances of *multiple function*, and therefore have to test not for a *substance* but for a *group*. When the substituent groups are determined the substance is identified by further investigation (*e.g.* m.p.). Thus a substance may react both as a phenol and as an aldehyde. Further experiments are necessary to find which of the hydroxyaldehydes it is.

**Additional Preliminary Tests** (see also p. 155).

(1) *Note colour and odour.* All nitro compounds and quinones are yellow. Most hydrocarbons, phenols, nitro-derivatives of hydrocarbons and aldehydes possess distinctive odours. The yellow colour of a nitro compound is usually intensified by alkali.

(2) *Investigate the solubility* of the substance in sodium carbonate and hydroxide and in dilute hydrochloric acid if it is insoluble in water. If soluble in the carbonate it is an acid, nitro- or chlorophenol. If insoluble in carbonate but soluble in caustic alkali it is a phenol. If it is soluble in dilute hydrochloric acid it is an amine.

(3) In the latter case cool and add a little sodium nitrite solution. If nothing separates (from secondary or tertiary

amine), pour the solution into one of β-naphthol in caustic soda. A red precipitate of an azo dye indicates a primary amine.

(4) If a phenol is suspected, try to couple it in caustic soda solution with diazotised aniline.

(5) If a nitro compound is suspected, reduce it with hot stannous chloride and apply the carbylamine or diazotisation tests. If necessary, extract with ether after making alkaline.

(6) Distil with zinc dust and smell the vapours evolved.

A. **Carbon and Hydrogen.**

(1) **Aromatic Hydrocarbons.**—Benzene, Toluene, Xylenes, Naphthalene, Anthracene. The first four may be recognised by their odour. The last two, when mixed in alcoholic and acetic acid solutions respectively with similar solutions of picric acid, deposit crystalline picrates (yellow and red respectively) of definite melting-point. The others are identified by their boiling-points.

(2) **Phenols.**—Phenol, cresols, catechol, guaiacol, resorcinol, quinol, pyrogallol, naphthols, alizarin, and also phenolic acids, aminophenols, etc.

Monohydric phenols are only slightly soluble in water. Di- and trihydric phenols are readily soluble, reduce ammoniacal $AgNO_3$, and their alkaline solutions blacken on exposure to air.

Monohydric phenols and resorcinol give purple colorations with ferric chloride. Thymol, *p*-oxyacids and nitrophenols give no colour. Catechol and its derivatives give a green colour, while quinol is oxidised, giving a yellow solution with a pungent odour of quinone.

If resorcinol is heated with phthalic anhydride and a drop of strong sulphuric acid and the product dissolved in alkali, an intense green fluorescence is obtained. Phenol under similar conditions gives a red solution (phenol phthalein) and catechol and pyrogallol, blue solutions. Bromine water usually gives a white precipitate of a di- or tribromo derivative of definite melting-point.

Phenols and naphthols in alkaline solution couple with

diazonium salts, yielding azo dyestuffs. Benzeneazo α-naphthol is soluble in NaOH, while the β compound is insoluble.

Alizarin is characterised by the intense purple colour of its sodium salt.

Phenols are frequently characterised by the melting-points of their benzoyl derivatives, which are most readily prepared by the *Schotten-Baumann reaction.* The phenol is dissolved in caustic soda and shaken with its own weight of benzoyl chloride for ten minutes. The precipitated benzoate is filtered off, washed, dried, re-crystallised from alcohol and the melting-point determined.

(3) **Ethers.**—These are characterised by their odour and non-reactivity, though, if a reactive group still remains, as in guaiacol or phenetidine, the substance gives the reactions of this group. Ethers are decomposed by refluxing with hydriodic acid, the phenol being isolated from the product by extraction with ether.

(4) **Alcohols.**—The only common alcohol is *benzyl alcohol*, a liquid with a faint characteristic odour. It is sparingly soluble in water and with warm chromic acid mixture gives benzaldehyde. The acetate is a fragrant-smelling liquid.

(5) **Aldehydes.**—The chief are benzaldehyde, nitrobenzaldehyde, anisaldehyde, salicylaldehyde, cinnamic aldehyde and vanillin. They are all recognisable by their odours. They possess the usual aldehyde reactions (except that of colouring Schiff's solution), and may be readily oxidised by chromic acid mixture to the corresponding acid. They can be characterised further by conversion into the phenyl hydrazone.

(6) **Ketones.**—The chief ketones are acetophenone, benzophenone and benzil. The first two are characterised by their odour and by the melting-points of their phenylhydrazones.

*Benzil* is a very non-reactive substance crystallising in yellow needles.

(7) **Quinones.**—These are yellow solids.

*Benzoquinone* is a yellow solid giving a violet-brown aqueous solution. It is readily recognised by its pungent odour. Sulphurous acid reduces it to quinol.

*Anthraquinone* forms pale yellow needles. On reduction with zinc dust and warm caustic soda the deep red sodium salt of oxanthranol is produced. Anthraquinone in its physical and chemical properties resembles a diketone and not a true quinone.

(8) **Acids.**—Most of the aromatic acids are sparingly soluble in cold water though they all dissolve in boiling water. Phthalic acid is moderately soluble in cold water. All except the oxybenzoic acids give in neutral solution a buff-coloured precipitate with ferric chloride.

On heating with soda-lime the carboxyl group is eliminated.

Acids are best identified by their melting-points or by the odours of their ethyl esters (made by heating with alcohol and sulphuric acid).

*Salicylic acid* gives a purple colour with ferric chloride.

*p-Oxybenzoic acid* gives no such coloration, but with boiling strong HCl yields phenol. Bromine water precipitates tribromophenol.

*Cinnamic acid* decolorises bromine water. Warm alkaline permanganate oxidises it to benzaldehyde and dilute nitric acid to benzoic acid.

*Phthalic acid* yields needles of the anhydride on distillation. With resorcinol and strong $H_2SO_4$ it gives fluorescein.

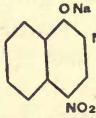
*Phthalic anhydride* forms long needles and gives an intense fluorescein reaction. On boiling with water it is slowly converted into the acid.

(9) **Esters.**—Most of these are liquids or solids of low melting-point and characteristic odour. They are identified by their hydrolysis products. Phenolic esters are best hydrolysed by 80 per cent. sulphuric acid. Phenyl and $\beta$-naphthyl salicylates (salol and betol) are of commercial importance as mild antiseptics.

B. **Carbon, Hydrogen and Nitrogen.**

(1) **Nitro Compounds.**—These are all yellow, the colour being intensified by alkali. Non-volatile nitro compounds deflagrate on

heating. Nitro compounds are reduced to amines by heating with stannous chloride and hydrochloric acid. If a metal is present, salts of nitrophenols or nitronaphthols are probably present. Sodium *o*-nitrophenate forms red needles, while the para compound is yellow.

*Martius' Yellow*, 

, and its sulphonic acid *Naphthol Yellow* are important yellow dyestuffs.

The nitrophenols give no colour with ferric chloride nor do they readily couple with diazonium salts.

(2) **Azo Compounds.**—These are all coloured, generally yellow, red or brown. They dissolve in strong sulphuric acid, giving intensely coloured solutions.

Azo compounds are reduced by hot stannous chloride solution to a mixture of amines.

(3) **Hydrazines.**—Phenylhydrazine, the only common member of this series, is usually met with as a yellow or brown oil with a peculiar characteristic basic odour. When pure it is a white crystalline solid. It is a powerful reducing agent, reacting with Fehling's solution to give cuprous oxide, nitrogen and benzene. The hydrochloride is a white crystalline solid somewhat sparingly soluble in water. If phenyl hydrazine is ground with potassium cyanate and acetic acid added to the mixture, phenyl semicarbazide (m.p. 172°) is formed.

(4) **Amines.**

*Primary Amines.*—These are insoluble in water but soluble in dilute acids. Most of them give the carbylamine reaction and may be diazotised and coupled with β-naphthol. Bromine yields insoluble bromo derivatives. Primary amines are best characterised by means of their acetyl derivatives, which are prepared by boiling with acetic anhydride and extracting with water.

*p-Toluidine* is the only simple mono-primary amine of the benzene series which is solid at ordinary temperatures.

The sulphates of primary amines are sparingly soluble in cold water and benzidine sulphate is practically insoluble.

Aminophenols and diamines blacken in alkaline solution on exposure to air.

*Secondary Amines.*—With the exception of diphenylamine these are liquids with a basic and slightly fishy odour. When the hydrochloric acid solution is treated with sodium nitrite a yellow oily nitrosamine is precipitated. (Apply the Liebermann test, p. 164.)

A warm solution of *diphenylamine* in strong sulphuric acid acquires an intense blue colour in the presence of a trace of nitrous or nitric acids. Secondary amines may be readily characterised by means of their acetyl or benzoyl derivatives.

*Tertiary Amines.*—Dimethylaniline and diethylaniline are the most common. They are liquids with a basic and slightly fishy odour. In acetic acid solution they couple with diazonium salts. Nitrous acid precipitates from a hydrochloric acid solution the yellow hydrochloride of a *p*-nitroso compound. This is decomposed by alkali, giving the green nitroso compound, and on heating evolves a dialkylamine. Tertiary amines unite with methyl iodide with evolution of heat, giving a solid quaternary ammonium salt.

*Aminophenols.*—These are solids, soluble in acids and alkalis and possesses the characteristic properties both of amines and of phenols. The *para* compound is the most common. Its alkaline solution blackens on exposure to air. Its ethyl ether, *phenetidine*, is a viscous oil which blackens on exposure to air. Acetyl phenetidine (*phenacetin*), an important drug, is a white crystalline solid.

*Amino Acids.*

*Anthranilic acid* is a yellow crystalline solid which behaves both as an amine and as an acid. On distillation with lime it yields aniline.

*Hippuric acid* forms stout white prisms, soluble in hot water. Boiling concentrated hydrochloric acid hydrolyses it to benzoic acid and glycine. The former crystallises on cooling and the filtrate after neutralisation gives the copper sulphate reaction for glycine (p. 163).

(5) **Anilides and Derivatives.**—These are white crystalline solids of definite melting-point, insoluble in cold water and fairly easily in boiling water. They are identified by hydrolysing with hot strong hydrochloric acid, cooling, filtering off any insoluble acid (*e.g.* benzoic acid), making alkaline and separating the amine by filtration or ether extraction. If the acid produced is soluble in water the alkaline solution should be boiled to expel ether, neutralised, and special tests applied for suspected acids.

*Carbanilide* is only hydrolysed by 80 per cent. sulphuric acid, while *oxanilide* is only decomposed by fusion with potash when aniline, phenyl isocyanide and a little potassium oxalate are formed.

(6) **Amides.**—These are solids readily hydrolysed by boiling acids or alkalis.

*Benzamide* and *salicylamide* are the most common.

*Phenylurethane* forms hard white prisms hydrolysed by alkalis to carbonic acid, alcohol and aniline.

(7) **Imides.**

*Phthalimide* forms white needles soluble in caustic soda (forming sodium phthalimide). Boiling alkalis hydrolyse it to ammonia and phthalic acid. It gives the fluorescein reaction.

*Phthalanil* forms white leaflets and is hydrolysed by boiling 60 per cent. sulphuric acid to aniline and phthalic acid. It gives the fluorescein reaction.

(8) *Nitriles.*—The only common nitrile is *benzonitrile*, a liquid with a smell resembling those of nitrobenzene and benzaldehyde. It is hydrolysed by hydrochloric acid to ammonia and benzoic acid.

C. **Carbon, Hydrogen and Halogen.**

(1) **Aryl Halides.**

*Chloro- and bromobenzene* are colourless liquids with an aromatic odour and are very non-reactive. The boiling-point is the best test.

*Chloro- and bromonaphthalene* resemble the benzenoid halides but have an odour of naphthalene.

*Benzyl chloride* is a liquid with a pungent odour and a very irritating action on the eyes and skin. It is converted into benzaldehyde by boiling with lead nitrate solution.

(2) **Acid Chlorides.**

*Benzoyl chloride* is a liquid with a characteristic pungent odour. It is slowly decomposed by water, forming benzoic and hydrochloric acids. It may be readily characterised by converting it into benzanilide or phenyl benzoate.

(3) **Halogen-substituted Phenols or Acids.**

The *chlorophenols* resemble phenol but dissolve in sodium carbonate solution. The ortho compound is liquid and the para solid.

Sym. *Tribromophenol* forms white needles melting at 92°. It is formed by the action of bromine on phenol and on *p*-oxybenzoic acid.

D. **Carbon, Hydrogen and Sulphur** (usually **Metal**).

(1) *Benzene, naphthalene and naphthol sulphonic acids.* These are nearly always given in the form of a salt. Fusion with caustic potash (not soda) yields a phenol (as potassium salt) and potassium sulphite. Of the naphthol sulphonic acids the chief is R acid (β-naphthol-3.6-disulphonic acid). It dissolves in alkali with a blue fluorescence.

(2) *Aldehyde bisulphite compounds.* Decompose by acid or alkali and extract the aldehyde with ether.

E. **Carbon, Hydrogen, Nitrogen and Sulphur.**

Either aminosulphonic acids, sulphates of amines or sulphonic acids of azo compounds.

*Aminosulphonic acids* are soluble in alkali and char on heating without melting. They may be diazotised and coupled with β-naphthol. The chief are metanilic, sulphanilic and naphthionic acids.

*Sulphates of amines* have an acid reaction, are sparingly soluble in cold water, give a sulphate reaction with barium chloride and are immediately decomposed by alkali.

*Sulphonated azo compounds* are highly coloured and are usually soluble in water. On reduction with stannous chloride the colour is discharged. (See Azo compounds, p. 169.)

F. **Carbon, Hydrogen, Nitrogen and Halogen.**

Either halogen-substituted nitrogen compounds (probably nitro or amino compounds) or salts of bases with halogen acids.

The former usually, though not invariably, give the reactions of the nitrogenous group. (Tribromoaniline has none of the typical properties of an amine.)

The salts of amines are acid in reaction, very soluble and are immediately decomposed by alkali. They give the ionic reaction of the halogen acid.

# APPENDIX IV

## SPECIFIC GRAVITIES OF COMMON LIQUIDS AT ORDINARY TEMPERATURES

| Substance | Wt. of 1 c.c. in grms. | Vol. of 1 grm. in c.c. | Substance | Wt. of 1 c.c. in grms. | Vol. of 1 grm. in c.c. |
|---|---|---|---|---|---|
| Acetaldehyde | ·78 | 1·28 | Formic acid | 1·22 | ·82 |
| Acetic acid | 1·05 | ·95 | Glycerol | 1·26 | ·79 |
| Acetic anhydride | 1·05 | ·95 | Ligroin | ·72 | 1·39 |
| Acetone | ·79 | 1·27 | Methyl alcohol | ·80 | 1·25 |
| Acetophenone | 1·03 | ·97 | Methylaniline | ·97 | 1·03 |
| Acetyl chloride | 1·10 | ·91 | Methyl iodide | 2·15 | ·47 |
| Amyl alcohol | ·81 | 1·24 | Nitrobenzene | 1·20 | ·83 |
| Amyl nitrite | ·90 | 1·11 | *o*-Nitrotoluene | 1·17 | ·85 |
| Aniline | 1·02 | ·98 | Paraldehyde | ·99 | 1·01 |
| Benzaldehyde | 1·05 | ·95 | Petroleum ether | ·65 | 1·54 |
| Benzene | ·88 | 1·14 | Phenylhydrazine | 1·09 | ·92 |
| Benzotrichloride | 1·38 | ·72 | Pyridine | ·99 | 1·01 |
| Benzoyl chloride | 1·21 | ·83 | Quinoline | 1·10 | ·91 |
| Benzyl chloride | ·95 | 1·05 | Toluene | ·86 | 1·16 |
| Bromobenzene | 1·50 | ·67 | *o*-Toluidine | 1·00 | 1·00 |
| Carbon disulphide | 1·26 | ·79 | Xylene | ·87 | 1·15 |
| Carbon tetrachloride | 1·60 | ·63 | | | |
| Chlorobenzene | 1·11 | ·90 | Bromine | 3·14 | ·32 |
| Chloroform | 1·50 | ·67 | Caustic potash (50%) | 1·55 | ·65 |
| Dimethylaniline | ·96 | 1·04 | Hydrochloric acid (conc.) | 1·16 (100 c.c. contains about 36 grms. H Cl.) | ·86 |
| Dimethyl sulphate | 1·32 | ·76 | | | |
| Ethyl acetate | ·88 | 1·14 | | | |
| Ethyl acetoacetate | 1·03 | ·97 | | | |
| Ethyl alcohol | ·79 | 1·27 | | | |
| Ethylene dibromide | 2·17 | ·46 | Nitric acid (conc.) | 1·42 | ·70 |
| Ethyl ether | ·72 | 1·39 | Nitric acid (fuming) | 1·50 | ·67 |
| Ethyl iodide | 1·94 | ·52 | Sulphuric acid (conc.) | 1·84 | ·54 |
| Ethyl malonate | 1·07 | ·93 | | | |

# APPENDIX V

## MELTING AND BOILING POINTS

## ALIPHATIC COMPOUNDS

| Substance | M.P. | B.P. |
|---|---|---|
| **Halogen Compounds** | | |
| Methyl chloride | | −23 |
| Methyl bromide | | 4 |
| Methyl iodide | | 43 |
| Ethyl chloride | | 12 |
| Ethyl bromide | | 38 |
| Ethyl iodide | | 72 |
| iso Propyl iodide | | 89 |
| iso Butyl chloride | | 68 |
| iso Butyl bromide | | 92 |
| iso Amyl chloride | | 100 |
| iso Amyl bromide | | 120 |
| Allyl iodide | | 103 |
| Methylene chloride | | 42 |
| Ethylene dichloride | | 84 |
| Ethylene dibromide | | 132 |
| αα-Dichlorhydrin | | 174 |
| Chloroform | | 61 |
| Bromoform | | 151 |
| Iodoform | 119 | |
| Carbon tetrachloride | | 78 |
| Acetylene tetrachloride | | 147 |
| Hexachlorethane | 184 in S.T. | |
| **Alcohols** | | |
| Methyl alcohol | | 66 |
| Ethyl alcohol | | 78 |
| *n*-Propyl alcohol | | 97 |
| iso Butyl alcohol | | 107 |
| iso Amyl alcohol | | 131 |
| Allyl alcohol | | 96 |
| Glycol | | 197 |
| Glycerol | | 290 |

| Substance | M.P. | B.P. |
|---|---|---|
| **Ethers** | | |
| Methyl ether | | −24 |
| Ethyl ether | | 35 |
| Amyl ether | | 173 |
| **Aldehydes and Derivatives** | | |
| Formaldehyde | | −21 |
| Paraformaldehyde | 171 | |
| Acetaldehyde | | 21 |
| Paraldehyde | | 124 |
| Chloral | | 97 |
| Chloral hydrate | 57 | |
| **Ketones and Derivatives** | | |
| Acetone | | 56 |
| Methyl ethyl ketone | | 80 |
| Sulphonal | 126 | |
| **Acids** | | |
| Formic acid | 9 | 101 |
| Acetic acid | 16 | 118 |
| Butyric acid | | 162 |
| iso Valeric acid | | 174 |
| Palmitic acid | 62 | |
| Stearic acid | 70 | |
| Oleic acid | 14 | |
| Chloracetic acid | 62 | 186 |
| Trichloracetic acid | 52 | 195 |

## ALIPHATIC COMPOUNDS—*continued*

| Substance | M.P. | B.P. |
|---|---|---|
| Aminoacetic acid (Glycine) | 232 | |
| Lactic acid | | decomp. |
| Oxalic acid, $2H_2O$ | 101 | |
| Oxalic acid (anhydrous) | 189 | |
| Malonic acid | 132 | |
| Succinic acid | 185 | |
| Tartaric acid | 170 | |
| Citric acid | 147 | |
| **Amides, Imides and Nitriles** | | |
| Formamide | | 208 |
| Acetamide | 82 | 222 |
| Carbamide | 132 | |
| Oxamide | decomp. | |
| Succinamide | 243 | |
| Succinimide | 126 | |
| Acetonitrile | | 82 |
| **Acid Chlorides and Anhydrides** | | |
| Acetyl chloride | | 55 |
| Acetic anhydride | | 138 |
| Succinic anhydride | 120 | |
| Carbon disulphide | | 46 |

| Substance | [α]D | M.P. | B.P. |
|---|---|---|---|
| **Esters** (*see* Table, p. 180) | | | |
| Methyl tartrate | | 48 | 280 |
| Methyl sulphate | | | 188 |
| Ethyl acetoacetate | | | 181 |
| Ethyl malonate | | | 197 |
| Ethyl succinate | | | 216 |
| Ethyl sulphate | | | 118 i.v. |
| Ethyl tartrate | | | 280 |
| iso Amyl nitrite | | | 96 |
| Allyl isothiocyanate | | | 151 |
| Tripalmitin | | 62 | |
| Tristearin | | 71 | |
| Glyceryl tribenzoate | | 69 | |
| **Carbohydrates and Derivatives** | | | |
| Glucose (hydrated) | +105 fresh | 86 | |
| Glucose (anhydrous) | ↓ +52·5 | 146 | |
| Fructose | −95·5 | 95 | |
| Maltose | +139 | decomp. | |
| Lactose | +52·5 | 205 | |
| Sucrose | +66·5 | 160 | |
| Invert sugar | −21·4 | | |
| Glucosazone | | 205 | |
| Maltosazone | | 206 | |
| Lactosazone | | 200 | |

## AROMATIC COMPOUNDS

| Substance | M.P. | B.P. |
|---|---|---|
| **Hydrocarbons and Derivatives** | | |
| Benzene | 4 | 80 |
| Toluene | −90 | 110 |
| *o*-Xylene | | 142 |
| *m*-Xylene | | 139 |
| *p*-Xylene | 15 | 138 |
| Cumene | | 153 |
| ψ-Cumene | | 169 |
| *p*-Cymene | | 175 |
| Mesitylene | | 164 |
| Diphenyl | 71 | |
| Diphenylmethane | 26 | 263 |
| Triphenylmethane | 92 | 330 |
| Naphthalene | 80 | 218 |
| Anthracene | 214 | 351 |
| Phenanthrene | 99 | 340 |
| Naphthalene picrate | 149 | |
| Anthracene picrate | 138 | |
| Phenanthrene picrate | 143 | |

## AROMATIC COMPOUNDS—*continued*

| Substance | M.P. | B.P. |
|---|---|---|
| **Aryl Halides** | | |
| Chlorobenzene | | 132 |
| Bromobenzene | | 155 |
| Iodbenzene | | 188 |
| *p*-Dibromobenzene | 89 | 219 |
| Benzyl chloride | | 178 |
| Benzal chloride | | 204 |
| Benzotrichloride | | 213 |
| *o*-Chlorotoluene | | 156 |
| *p*-Chlorotoluene | | 163 |
| *m*-Chloronitrobenzene | 44 | |
| *p*-Chloronitrobenzene | 83 | |
| *m*-Bromonitrobenzene | 56 | |
| *p*-Bromonitrobenzene | 126 | |
| α-Chloronaphthalene | | 263 |
| α-Bromonaphthalene | | 279 |
| **Nitro Compounds** | | |
| Nitrobenzene | | 206 |
| *o*-Nitrotoluene | | 216 |
| *p*-Nitrotoluene | 54 | 230 |
| *m*-Dinitrobenzene | 90 | |
| *m*-Dinitrotoluene | 71 | |
| α-Nitronaphthalene | 61 | |
| **Phenols and Derivatives** | | |
| Phenol | 42 | 182 |
| *o*-Cresol | 30 | 188 |
| *m*-Cresol | | 201 |
| *p*-Cresol | 36 | 198 |
| *o*-Chlorophenol | | 176 |
| *p*-Chlorophenol | 37 | 217 |
| Tribromophenol | 92 | |
| *p*-Nitrosophenol | 126 | |
| *o*-Nitrophenol | 45 | |
| *p*-Nitrophenol | 114 | |
| *m*-Dinitrophenol | 114 | |
| Picric acid | 122 | |
| *p*-Aminophenol | 184 | |
| Phenol phthalein | 253 | |

| Substance | M.P. | B.P. |
|---|---|---|
| Eugenol | | 252 |
| Carvacrol | | 236 |
| Thymol | 44 | 230 |
| Catechol | 104 | |
| Guaiacol | 28 | 208 |
| Resorcinol | 118 | |
| Quinol | 169 | |
| Phloroglucinol | 219 | |
| Pyrogallol | 132 | |
| α-Naphthol | 95 | 278 |
| β-Naphthol | 122 | 286 |
| Alizarin | 290 | |
| Purpurin | 253 | |
| **Phenolic Ethers and Esters** | | |
| Anisol | | 154 |
| Phenetol | | 172 |
| *o*-Anisidine | | 228 |
| *p*-Anisidine | 56 | 246 |
| *p*-Phenetidine | | 253 |
| Guaiacol | 28 | 208 |
| Anethol | 21 | 232 |
| Phenyl acetate | | 195 |
| *o*-Cresyl acetate | oil | |
| *m*-Cresyl acetate | oil | |
| *p*-Cresyl acetate | | 210 |
| Phenacetin | 134 | |
| Resorcinyl diacetate | | 273 |
| Quinol diacetate | 123 | |
| Eugenyl acetate | 31 | 270 |
| α-Naphthyl acetate | 49 | |
| β-Naphthyl acetate | 70 | |
| Alizarin diacetate | 180 | |
| Phenyl benzoate | 69 | |
| *o*-Cresyl benzoate | oil | |
| *m*-Cresyl benzoate | 38 | |
| *p*-Cresyl benzoate | 71 | |
| Guaiacol benzoate | | |
| Resorcinyl dibenzoate | 117 | |
| α-Naphthyl benzoate | 56 | |
| β-Naphthyl benzoate | 107 | |
| Phenyl salicylate | 42 | |
| β-Naphthyl salicylate | 132 | |

## AROMATIC COMPOUNDS—*continued*

| Substance | M.P. | B.P. |
|---|---|---|
| **Glucosides** | | |
| Salicin | 201 | |
| Amygdalin | 200 | |
| Phloridzin | 109 | |
| **Alcohols** | | |
| Benzyl alcohol | | 206 |
| Benzhydrol | 68 | 298 |
| Triphenylcarbinol | 159 | |
| **Esters** (*see* p. 180) | | |
| Phenyl mustard oil | | 222 |
| **Aldehydes and Derivatives** | | |
| Benzaldehyde | | 179 |
| *o*-Nitrobenzaldehyde | 44 | |
| *m*-Nitrobenzaldehyde | 58 | |
| Salicylaldehyde | | 196 |
| *p*-Oxybenzaldehyde | 115 | |
| Anisaldehyde | | 248 |
| Vanillin | 80 | |
| Cinnamic aldehyde | | 247 |
| Benzoin | 137 | |
| α-Benzaldoxime | 34 | 220 |
| Benzaldehyde phenylhydrazone | 152 | |
| *m*-Nitrobenzaldehyde ,, | 121 | |
| Salicylaldehyde ,, | 143 | |
| *p*-Oxybenzaldehyde ,, | 178 | |
| Anisaldehyde ,, | 121 | |
| Vanillin ,, | 105 | |
| Cinnamic aldehyde ,, | 168 | |
| **Ketones and Quinones** | | |
| Acetophenone | 20 | 202 |
| Benzophenone | 46 | |
| Michler's ketone | 172 | |
| Benzoin | 137 | |
| Benzil | 95 | |
| Quinone | 116 | |
| Chloranil | subl. | |
| Anthraquinone | 285 | |
| Phenanthraquinone | 200 | |
| Acetophenone phenylhydrazone | 105 | |
| Benzophenone phenylhydrazone | 137 | |
| **Nitriles** | | |
| Benzonitrile | | 191 |
| Benzyl cyanide | | 232 |
| Mandelonitrile | | decomp. |
| **Amides and Imides** (*see* also Anilides) | | |
| Benzamide | 128 | |
| Salicylamide | 138 | |
| Phthalimide | 230 | |
| Phthalanil | 205 | |
| Thiocarbanilide | 152 | |
| Phenylurethane | 52 | |
| Saccharin | 200 | |
| **Acids** | | |
| Benzoic acid | 121 | |
| *m*-Bromobenzoic acid | 155 | |
| *m*-Nitrobenzoic acid | 141 | |
| Anthranilic acid | 145 | |
| Salicylic acid | 156 | |
| Acetyl salicylic acid | 134 | |
| *p*-Oxybenzoic acid | 210 | |
| Anisic acid | 184 | |
| Phenylacetic acid | 77 | |
| Mandelic acid | 118 | |
| Gallic acid | 220 | |
| Hippuric acid | 187 | |
| Cinnamic acid | 133 | |
| Phthalic acid | 210*ca.* | |
| Terephthalic acid | subl. | |

## AROMATIC COMPOUNDS—*continued*

| Substance | M.P. | B.P. |
|---|---|---|
| **Acid Chlorides and Anhydrides** | | |
| Benzoyl chloride | | 198 |
| Phthalyl chloride | | 275 |
| Benzoic anhydride | 42 | 360 |
| Phthalic anhydride | 128 | |
| Coumarin | 70 | |
| **Azoxy, Azo and Hydrazo Compounds** | | |
| Azoxybenzene | 36 | |
| Azobenzene | 68 | 293 |
| Benzeneazophenol | 152 | |
| Benzeneazo α-naphthol | 206 | |
| Benzeneazo β-naphthol | 134 | |
| Benzeneazoaniline | 125 | |
| Diazoaminobenzene | 98 | |
| Benzeneazodimethylaniline | 116 | |
| Benzeneazo *m*-phenylenediamine | 115 | |
| Hydrazobenzene | 131 | |
| **Amines** | | |
| Aniline | | 184 |
| *m*-Chloraniline | | 230 |
| *p*-Chloraniline | 70 | 230 |
| *p*-Bromaniline | 63 | |
| Tribromaniline | 119 | |
| *o*-Nitraniline | 71 | |
| *m*-Nitraniline | 114 | |
| *p*-Nitraniline | 147 | |
| *o*-Toluidine | | 197 |
| *p*-Toluidine | 45 | 198 |
| Methylaniline | | 192 |
| Nitrosomethylaniline | | decomp. |
| Dimethylaniline | | 192 |
| *p*-Nitrosodimethylaniline | 85 | |
| Ethylaniline | | 206 |
| Diethylaniline | | 213 |
| Diphenylamine | 54 | 310 |
| *m*-Phenylenediamine | 63 | 277 |
| Benzidine | 122 | |
| Tolidine | 112 | |
| α-Naphthylamine | 50 | 300 |
| β-Naphthylamine | 112 | 294 |
| *p*-Aminophenol | 184 | |
| *p*-Anisidine | 56 | 246 |
| *p*-Phenetidine | | 248 |
| Phenylhydrazine | 23 | 241 |
| **Anilides and Derivatives** | | |
| Formanilide | 46 | 284 |
| Acetanilide | 112 | 304 |
| Carbanilide | 235 | |
| Thiocarbanilide | 152 | |
| Phenylurethane | 52 | |
| Oxanilide | 245 | |
| Benzanilide | 163 | |
| *m*-Chloracetanilide | 73 | |
| *p*-Chloracetanilide | 173 | |
| *o*-Bromacetanilide | 99 | |
| *p*-Bromacetanilide | 166 | |
| *o*-Nitracetanilide | 93 | |
| *m*-Nitracetanilide | 150 | |
| *p*-Nitracetanilide | 207 | |
| Acet *o*-toluidide | 109 | |
| Acet *p*-toluidide | 147 | |
| Acetyl methylaniline | 101 | |
| Acetyl ethylaniline | 55 | |
| Acetyl diphenylamine | 103 | |
| sym Diacetylbenzidine | 317 | |
| sym Diacetyltolidine | 315 | |
| Acetyl α-naphthylamine | 159 | |
| Acetyl β-naphthylamine | 132 | |
| Phenacetin | 134 | |
| *p*-Brombenzanilide | 202 | |
| *o*-Nitrobenzanilide | 94 | |
| *m*-Nitrobenzanilide | 156 | |
| *p*-Nitrobenzanilide | 199 | |
| Benz. *o*-toluidide | 131 | |
| Benz. *p*-toluidide | 158 | |
| Benzoyl methylaniline | 63 | |
| Benzoyl ethylaniline | 60 | |
| Benzoyl diphenylamine | 177 | |
| Benzoyl α-naphthylamine | 156 | |
| Benzoyl β-naphthylamine | 143 | |

# APPENDIX VI

## MELTING AND BOILING POINTS OF COMMON ESTERS

*Melting points in italics*

| Alcohol. | Formate. | Acetate. | Butyrate. | iso Valerate. | Oxalate. | Benzoate. | Salicylate. | Cinnamate. | Phthalate. |
|---|---|---|---|---|---|---|---|---|---|
| Methyl . | 32 | 57 | 102 | 116 | *54*<br>164 | 199 | 224 | *34*<br>263 | 280 |
| Ethyl . | 54 | 76 | 121 | 134 | 186 | 211 | 227 | 270 | 295 |
| n-Propyl | 81 | 101 | 143 | 156 | 213 | 229 | 239 | 284 | ... |
| iso-Butyl | 98 | 116 | 158 | 169 | 225 | 234 | 270 | ... | ... |
| iso-Amyl | 123 | 139 | 176 | 188 | 265 | 261 | 270 | ... | ... |
| Phenyl . | ... | 195 | ... | ... | *130* | *69*<br>314 | *43* | *73* | *70* |
| Benzyl . | ... | 206 | 240 | ... | ... | *20*<br>323 | ... | *39* | ... |

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